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CONCENTRATED MINE DRAINAGE DISPOSAL INTO SEWAGE TREATMENT SYSTEMS

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PB 213 042

Concentrated Mine Drainage Disposal Into Sewage Treatment Systems

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Studies were undertaken on a small scale to determine the effect artificial iron-rich acid brines had on municipal sewage treatment processes. The brines were devised to simulate concentrates from treatment of acid mine drainage. At very high concentrations, the brines neutralized with lime give virtually complete removal of phosphate from primary effluent, activated sludge effluent, or anaerobic sludge digester decantate. The cost of the iron-rich acid brine produced from acid mine drainage by the reverse osmosis membrane treatment is estimated at $35/1000 gallons of brine or about 73¢/1000 gallons of acid water treated. Cost of transportation by rail, truck, and pipeline are also shown. (Smith-Texas)

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Richard M. Smith, Jr. | Texas Univ, Austin

Concentrated Mine Drainage Disposal

Into Sewage Treatment Systems

THE DISPOSAL OF ACID BRINES

FROM ACID MINE DRAINAGE IN

MUNICIPAL WASTEWATER TREATMENT

by

Environmental Research and Applications, Inc.
24 Danbury Road
Wilton, Connecticut 06897

for the

ENVIRONMENTAL PROTECTION AGENCY

Program #14010 FBZ
September, 1971

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ABSTRACT

The effect of artificial iron-rich acid brines on municipal sewage treatment processes was studied in small scale. The brines were devised to simulate concentrates from treatment of acid mine drainage. The processes included primary settling, activated sludge digestion, and other unit processes.

The raw brines even at a level of 20% vol/vol or higher do not interfere with primary settling, but activated sludge digestion is completely inhibited by the acid. The brines when neutralized with lime improve primary settling and the neutralized brines do not inhibit activated sludge. Filtration of all sewage fractions is improved by the lime-acid brine neutral mixture. At the very high concentrations used, the neutralized brines give virtually complete removal of phosphate from primary effluent, activated sludge effluent, or anaerobic sludge digester decantate.

Cost of reverse osmosis membrane treatment of acid mine drainage to produce the iron-rich acid brine is estimated to be in the range of 35¢/1000 gal. of brine corresponding to original 48,000 gal. of acid mine water or about 73¢ per thousand gallons of acid mine water treated. Engineering analysis and costs are shown for transporting the brine from the mine site to the sewage treatment plant by rail, truck, and pipeline over distances ranging from 10 to 50 miles. Transportation by pipeline involves per-mile costs on the order of 5¢/1000 gal. of brine.

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SECTION I

CONCLUSIONS

1. Many sites where acid mine drainage originates and degrades water quality will require on-site treatment.

2. The products of treatment are concentrated acid brines or brine-sludge mixtures and relatively pure water. Depending upon the method of treatment, the product water can be suitable for safe discharge to surface water courses or it can be a high grade water for industrial use.

3. The brines produced by treatment are not of sufficient value to pay for treatment by any known method, but they can be disposed of through municipal wastewater treatment plants where they will be of some value especially for sludge conditioning and nutrient removal.

4. Reverse osmosis offers an attractive method for on-site treatment.

5. It is economically feasible to transport acid brines from the mine sites to municipal wastewater treatment plants by pipeline.

6. Some aspects of the development of an optimum scheme for disposal of acid brines require further research especially nitrification, denitrification, hydrolysis, and ultimate sludge disposal.

SECTION II

RECOMMENDATIONS

1. Acid mine drainage sites should be inventoried or existing inventories should be studied to find a site suitable for installation of a pilot plant to produce acid brine (and pure water) for use at an accessible municipal wastewater treatment plant.

2. A pilot scale investigation of the disposal of acid brine at a municipal secondary wastewater treatment plant should be initiated. The recommended project could use artificial acid brine until the pilot plant brine becomes available.

3. Laboratory scale investigations of the use of acid brine for certain advanced wastewater treatment unit processes should be initiated. The processes should include biological nitrification and denitrification, sludge conditioning, alkaline hydrolysis and adsorption, and ozonation.

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SECTION III

INTRODUCTION

Acid mine drainage is a significant water pollution problem in many mining areas of the United States. Acid mine waters originate from the chemical oxidation of pyrites contained in coal and in shales and other rocks associated with coal deposits and pyritic ore bodies. In natural hydrographic regimes and especially in the regimes altered by mining and other excavations, acid water find their way into water courses. The acid and heavy metals in the drainage seriously damage the stream flora and fauna even to the point of local extinction of the biota. In the watercourse, acids are eventually neutralized through reactions with natural alkaline materials and the heavy metals are precipitated forming deposits of hydrous oxides of iron, aluminum and manganese. In the course of this natural self-purification, however, stretches of streams, miles in extent, can be degraded.

Objective of This Study

Various schemes for preventing the drainage of acid mine waters into water courses have been proposed and undertaken, but not all such problems can be economically solved by sealing the mine, diverting the flow, or other such approaches (1, 2, 3). From the standpoint of economic value, acid mine water are ordinarily too dilute and too heterogeneous for product recovery (acid, iron, other heavy metals) to be practical. Our study examined the feasibility of concentrating acid mine water by certain processes and transporting the concentrated brine to municipal waste treatment plants for disposal. The relatively pure water produced from the treatment process would be discharged to the local watercourse or used by a local municipality or industry. With this broad objective--disposal of concentrated acid brines via municipal wastewater treatment plants -- we undertook laboratory investigations of the effect of synthetic acid brine on primary and secondary sewage treatment processes.

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SECTION IV

REVIEW OF LITERATURE

Introduction

The term acid mine drainage (AMD) is applied to drainages which have an abnormally low pH value and to drainages which contain neutral substances such as ferrous sulfate. Acid drainage from coal mining operations usually contains sulfuric acid and ferrous, ferric, aluminum and manganese salts in fairly high concentrations and also calcium, magnesium and sodium salts, carbon dioxide and silicic acid.

Acid mine drainage is generated when the oxidation products of the pyrite contaminate the surface drainage and the ground waters drained from the mine. The feasibility of controlling the acidic contamination of coal mine drainage at the source has been studied, discussed and tried in the U.S.A. (4,5,6). Most of the suggested methods of control have been based on the principle of excluding the mutual contact of the three components of acid mine drainage: air, water, and pyrite. Some of the segregation methods proposed were: diversion of water from acid producing areas, exclusion of air from abandoned underground mines and covering the pyritic materials with non-acid forming materials in restored strip mine sites and refuse banks. It is evident from the physical nature of the sources of acid contamination of coal mine drainage that segregation will not be possible at some sites, and that complete segregation will be difficult at many. It will be particularly difficult to control the interaction of air, water, and pyrite in active underground mine workings. Therefore the acid mine drainage has to be treated after its formation and the cost of treatment is great. Thus there is an increasing demand for cheaper mine drainage treatment processes.

Acid Mine Drainage Treatment Processes

There are a number of processes reported in the literature for the treatment of acid mine drainage and these are described in brief as below:

1. Precipitation of Iron

   By adding alkaline neutralizing agents such as hydrated lime, sodium carbonate, and sodium hydroxide to acid solutions of ferrous iron, iron can be precipitated. Other methods would require expensive precipitating agents and are probably not economical for high concentrations of iron.

2. Electrolysis of Iron (II) Solutions

   Direct current hydrolysis of acidified iron (II) sulfate solutions

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produces a complex set of reactions and the three predominating reactions are shown below:

$H_2O \longrightarrow 1/2\ O_2 + 2H^+ + 2e^-$

$Fe^{+2} \longrightarrow Fe^{+3} + e^-$

$Fe^{+3} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^{+3}$

The rate of removal of iron from solutions depends on the current density at the electrode surface. $Fe(OH)_3$ deposits as a brown precipitate around the anode.

3. Aeration - Filtration

This is one of the most common methods used on a commercial scale for removing iron from aqueous solutions. The process consists of oxidation of iron (II) to iron (III) by aeration, followed by hydrolysis of iron (III) and subsequent filtration

$$Fe^{+3} + 3H_2O \longrightarrow Fe(OH)_3\ (Fe_2O_3 \cdot n\ H_2O) + 3H^+$$

Superficially this process appears inviting for application to AMD but many problems are involved. The two major ones are:

(i) conversion of Fe (II) to Fe (III) by air oxidation is slow in media where the pH is less than seven.

(ii) lime or $CaCO_3$ must be added to increase the pH. The conversion of Fe (II) to Fe (III) by aeration is more rapid at pH >7. However, for large volumes of AMD, neutralization would require large amounts of $CaCO_3$.

4. Ultrasonic Methods

The use of ultrasonic energy in the oxidation of acidified iron (II) sulfate has been investigated to a considerable extent with some promising results. The rate of oxidation of iron (II) by ultrasonic energy is a function of the intensity of the waves but the relationship appears to be non-linear. Ultrasonic energy may be useful in effecting coagulation of the hydrous iron (III) oxide formed by oxidation.

5. Ozone

Ozone treatment has been considered as a means of removing iron from aqueous solutions. A combination ozone-activated carbon system is presently in use for the removal of iron and manganese from drinking water. (7)

6. Irradiation and Photo-oxidation

Oxidation of iron (II) using alpha, beta and gama radiation has been studied and the mechanism is apparently the same as for ultrasonic oxidation. The reactions appear to be about four times faster in aerated water than in oxygen-free water. The problems associated are: yield of the reactions are not particularly high and the depth of penetration of the water by the irradiating particles is very short.

7. Lime Processes

The principle of the lime processes is that lime (calcium oxide or calcium hydroxide), or other strong alkali such as sodium hydroxide, is mixed with the acid mine drainage to neutralize the acids,

$$H_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2\ H_2O$$

and to precipitate the contaminating metal salts

$$Fe_2(SO_4)_3 + 3\ Ca(OH)_2 \longrightarrow 3\ CaSO_4 + 2\ Fe(OH)_3$$

The sludge formed by sedimentation from lime neutralization has a high water content and presents a difficult disposal problem. The cost of treatment by lime treatment is estimated at $1.09/1000 U.S. gallons (1). Hanna et al (4), in a review of the acid mine drainage problem, concluded that neutralization processes were not economically attractive except in specific cases involving small well-defined areas.

8. Limestone Processes

This process used the minerals, limestone and dolomite (ie $CaCO_3$, and $Mg/CaCO_3$), and the reaction with the acidic salt would be: $Fe_2(SO_4)_3 + 3\ CaCO_3 + 3\ H_2O \longrightarrow 3\ CaSO_4 + 2\ Fe(OH)_3 + 3\ CO_2$. An upflow expanded bed process using limestone for the treatment of acid wastes has been reported (8). Sulfuric acid in concentrations up to 5000 mg/l could be neutralized without inactivation of the limestone. The process was, however, stated to be unsuitable for the neutralization of wastes containing iron salts because of inactivation of the limestone.

There have been a number of cases (9,10,11) where the limestone processes have been used. From a critical review of literature, it is found that limestone has found application in the neutralization of acid wastes other than those containing iron and other precipitable salts, and that a considerable problem of limestone inactivation must be expected when these salts are present.

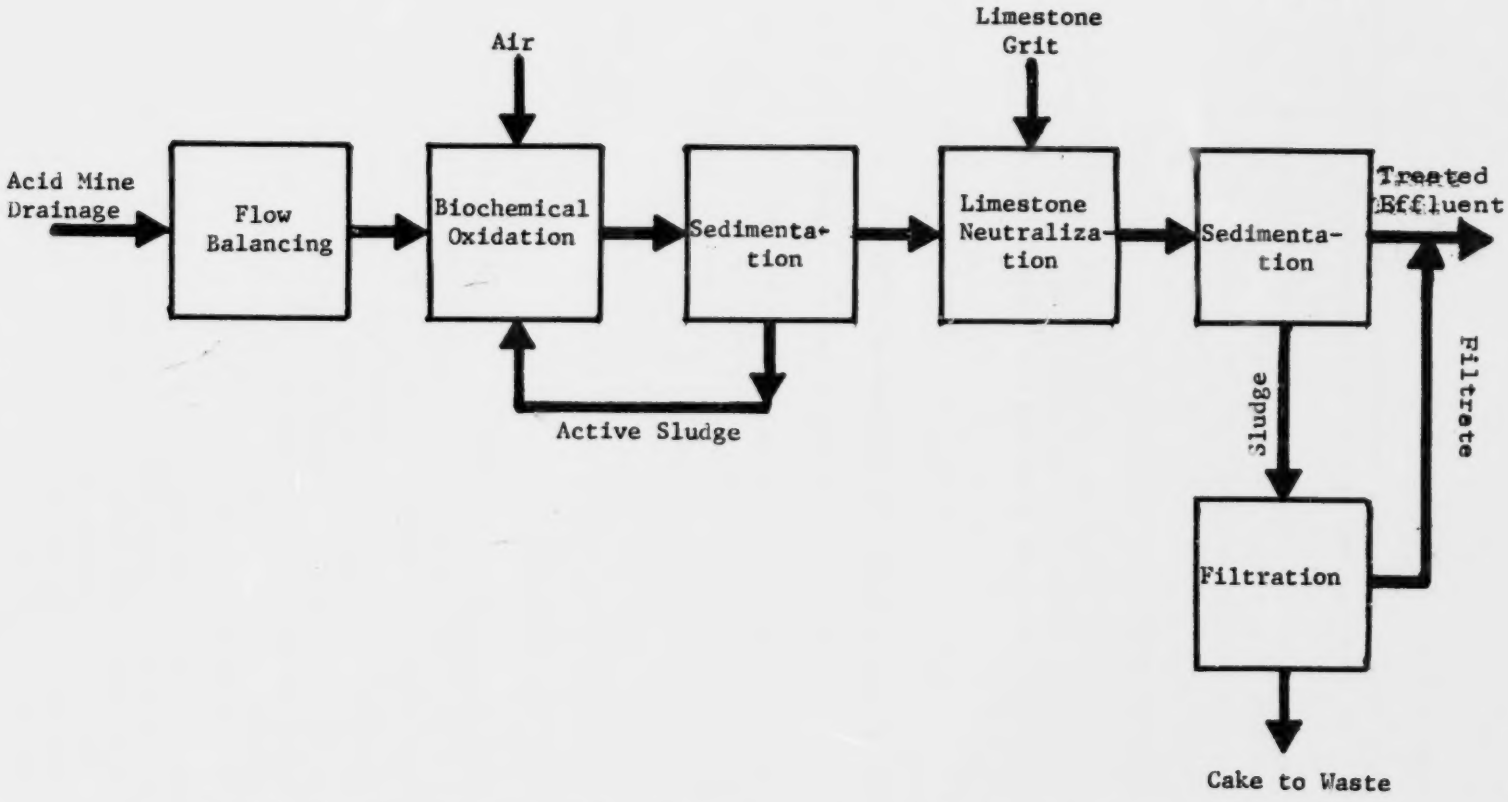

Figure 1. Flow Diagram of Complete Biochemical Oxidation and Limestone Neutralization Process

9. Biochemical Oxidation Processes

The simplest procedure to remove ferrous salts would be to oxidize the ferrous salts to ferric which could be removed together with the original ferric salts by the limestone. Atmospheric oxygen is by far the cheapest oxidant and is particularly attractive since an excess of air could not produce too high a redox potential in the treated drainage.

Unfortunately, atmospheric oxygen is not able to oxidize ferrous salts in acidic solution despite the fact that the free energy change is favorable (12). A micro organism capable of promoting the atmospheric oxidation of ferrous salts in acid solution has been widely reported in acid mine drainages (4, 13, 14). This micro organism is an autotrophic bacterium, and Silverman and Lundgren (15) reported the optimum growth temperature of this bacterium to be 28°C, the optimum ferrous concentration to be 9000 mg/l Fe, and the optimum pH range to be 2.5 to 4.0. The bacterium studied by Silverman and Lundgren could not oxidize manganous, nickelous, and cobaltous salts, but several authors have reported the tolerance of acidophilic ferrous oxidizing bacteria to metal ions such as manganese, copper, and zinc. (13) A scheme proposed in England (4) for the control of acid mine drainage pollution by biochemical oxidation and limestone neutralization treatment is shown in Figure 1. The outstanding characteristic of the complete process was the ease of control. The required supervision was minimal since over-treatment in the oxidation and neutralization stages could only be beneficial. The practicability of the whole process to the treatment of acid mine drainage has been demonstrated by this study. The limitations of this process are: the dissolved iron content should be at least 10 to 20 mg/l and a total acidity of at least 25 mg/l as ($CaCO_3$). The cost of treatment is estimated to range between $0.67 to $1.90 per 1000 gallons.

10. Foam Fractionation

A foam fractionation technique (16) has been developed by Garrett Research and Development Company, for removing phosphates and suspended solids and lowering chemical oxygen demand. The technique consists of treating the waste stream with ferric chloride or alum, then dissolving air in the water under high pressure (about 175 psi). When the pressure is released, micro-size bubbles produce a creamlike foam that effectively removes not only phosphates but also particulates in general and both soluble and insoluble organic matter.

Tests with wastewater obtained at a Pomona, California, sewage treatment plant showed that when alum or ferric chloride were used in concentrations of 300 to 400 mg/l, foam fractionation removed 90% of the phosphates and 80% of the suspended solids,

and lowered the chemical oxygen demand by 70%. Preliminary estimates for a 10 MGD foam - fractionation plant indicate a capital cost of $235,000 and an operating cost of 6¢/1000 gallons. The land area requirements are very low, in the order of half acre for a 10 MGD plant. As indicated in the preceding paragraphs, none of these processes has yet been shown to be less expensive for general application. In order to bring down the operating costs of the sewage treatment facilities, attention has been given to the use of waste materials, such as acid mine drainage. Iron salts act as flocculating agents in the primary and secondary clarification tanks. Iron salts act as an oxygen carrier in the activated sludge process and the effectiveness of the returned sludge is increased by the fact that sludge passing through the cycle more than once becomes richer in iron, aluminum, and other hydroxides and thus clarification of sewage and destruction of protein are accelerated. In general it can be assumed that iron may be helpful both as an oxygen carrier and as an adsorbent and coagulant. (17)

The effect of iron salts on the removal of BOD, SS, phosphate are discussed in the following sections:

Phosphate Removal by Iron

1. Elimination of Phosphate from Sewage

Phosphorus removal processes recently proposed are mostly based on precipitation, with cations forming insoluble phosphate salts, or on absorption by inorganic hydroxides. The reactions with Al^{3+}, Fe^{3+}, and Ca^{2+} or with combinations of Fe^{3+} and Ca^{2+} offer some economical possibility for the removal phosphorus.

In addition to these inorganic chemical reactions, a biological process might be considered theoretically, using the well-known property of many microorganisms to store phosphates as polyphosphates in their cells when phosphorylation substances are lacking. (18)

2. Iron (III) as precipitant

At pH$>$7, $FePO_4$ results as a product, whose solubility product is $K_s = 10^{-23}$ at 25°C (18). Excess of Fe (III) is required in the sewage treatment for the formation of a well-flocculating hydroxide precipitate which includes the $FePO_4$ particles. $FePO_4$ particles act as an efficient absorbent for organic phosphate compounds and eventually for polyphosphates.

Phosphate removal with Fe(III) has been considered exclusively as an absorption process. This hypothesis contradicts the opinion of Galal and Stumm, who favor a simple chemical precipitation mechanism. (19) However, from a practical point of view,

both reaction mechanisms lead to the same result and require the same operating conditions.

When treating an activated sludge plant effluent, the stoichiometrical requirement of Fe is 1.8 mg/l per mg/l P. However, for complete phosphate removal this has to be supplemented by at least 10 mg/l for hydroxide formation. There are two methods of applying the precipitants:

(1) Simultaneous precipitation
(2) Post precipitation

Simultaneous precipitation involves addition of the precipitant directly to the influent of the aeration basin, promoting the formation of hydroxide and binding of phosphates simultaneously. Post precipitation involves the addition of precipitants to the secondary effluents in a conventional manner. Both the methods of applications have been studied on a laboratory scale (20) and the following are the results:

A. Both processes required the addition of at least 20 mg/l Fe^{3+} for the reduction of phosphate from 7.15 mg/l to 0.5 mg/l or less.

B. $Fe(OH)_3$ flocculation in the simultaneous process was frequently incomplete, resulting in an opalescent final effluent with considerable carryover of colloidal $Fe(OH)_3$ and phosphorus.

C. The addition of Fe (III) to the activated sludge resulted in a striking change of the sludge biocenosis leading to better settling.

D. When the dosing was more than 10 mg/l Fe (III), the protozoan fauna disappeared completely within the first two days.

E. There was a remarkable increase of excess sludge volume in the simultaneous precipitation units in comparison to conventional treatment. (See Table 1)

TABLE 1

Excess Sludge Production in Simultaneous and Post Precipitation Units (gallons per gallon of sewage treated) for Various Dosage of Iron (20).

Dosage of Fe^{3+}	10 mg/l	20 mg/l	30 mg/l
Simultaneous Precipitation	0.5	0.62	0.50
Post Precipitation	0.41	0.28	0.25

According to the literature cited the hydroxide sludge formed is of poor settling and dewatering characteristics.

3. Removal of Phosphorus with Lime and Iron (III)

In order to reduce sludge solids production and excess sludge volume in the precipitation unit, a combination of phosphate precipitation with iron (III) and lime was tried. Iron was added at 1.8 mg/l Fe (III) for each mg/l of phosphate and lime added to raise the pH of the mixture to 8.8. This pH was selected so that considerable precipitation of $CaCO_3$ would take place, which might be helpful as a thickening aid of the iron hydroxide formed; at the same time the calcium carbonate was thought to act as an absorbent for colloidal $FePO_4$ and organic phosphate. The results of an experiment run for 30 days with the final effluent of an activated sludge plant demonstrated that phosphorus removal was equivalent to the efficiency achieved with lime or iron precipitation alone. Excess sludge quantity and sludge volume were much smaller but the settling property of sludge was poor. Essential factors to be considered for the operation of this process are: the amount of orthophosphate to be removed, the alkalinity, and the Ca hardness of the treated sewage. This combined process is expected to be the most economic over a wide range of conditions. The quantity of precipitation chemicals are moderate, and the sludge produced thickens rapidly and can be effectively dewatered to a highly concentrated slurry or a filter cake, which may be dumped without danger of secondary leaking of phosphorus.

Alum and Iron (III) precipitation have two disadvantages: the costs for the chemicals are relatively high, and the processes lead to a difficult sludge disposal problem. In the case of alum precipitation, the recovery of the precipitant as proposed by Lea et al (II), may lighten the cost burden to some degree.

(a) Phosphate Precipitation

The affinity between multivalent aqueous metal ions (Ca^{+2}, Fe^{+3}, Al^{+3}) and PO_4^{-3}, HPO_4^{-2} or polyphosphate is about 4 - 12K cal per mole. With simple solutions of orthophosphate, well defined reaction products such as $FePO_4 \cdot 2H_2O$ (Strengite) can be formed in accordance with the stoichiometry of the reaction. Organic phosphorus compounds are surface-active and may become adsorbed on precipitates and other interfaces, but counter-ion adsorption alone cannot account for the high removal efficiency because of the stoichiometry observed. A substantial fraction of the phosphorus in sewage is contained in the form of suspended matter; this fraction is removed by coagulation rather than by precipitation. Ferric salts are good coagulants and can be used to coagulate the phosphate colloids.

(b) Solubility Relations

The continuous precipitation of phosphate in treatment of wastes is a dynamic process; most likely, equilibrium conditions are not attained. The formulation of the stoichiometry of the chemical reaction defines the minimum requisite quantity of chemicals. The equilibria (21) that need to be considered are listed below:

1. Solubility equilibra

$$FePO_4 \cdot 2H_2O\ (s) \longrightarrow Fe^{+3} + PO^{-3} + 2H_2O$$
$$(\log K\ 25°C) = -23)$$

2. Acid - Base Equilibria

$$Fe^{+3} + OH^- \longrightarrow FeOH^{+2}$$

$$FeOH^{+2} + OH^- \longrightarrow Fe(OH)_2^+$$

$$Fe(OH)_2^+ + OH^- \longrightarrow Fe(OH)_3\ (s)$$

3. Complex Formation Equilibria

$$FeHPO_4^+ \longrightarrow Fe^{+3} + HPO_4^{-2}$$

$$FeH_2PO_4^{+2} \longrightarrow Fe^{+3} + H_2PO_4^-$$

$$Fe\ (HP_2O_7)_2^{-3} \longrightarrow Fe^{+3} + 2HP\ O_7^{-2}$$

(c) Kinetics of Phosphate Precipitation

Equilibrium calculations and experimental verification show, that $FePO_4$ (s) is a stable solid phase if phosphate is precipitated in the low pH range of 4 to 6 (See Figure 2). Precipitation of phosphate with Fe (III) is very fast. The rate of removal is controlled by agglomeration of colloids and by settling. Precipitation of phosphate by Fe (III) will be more efficient if the Fe (III) is produced by slow, homogeneous generation of ferric ion through the oxidation of ferrous ion, than it will be if Fe (III) as such is added to the wastewater. In the latter case, ferric ions, because of relatively high localized concentrations, tend to react (depending on pH) with OH^- ions rather than with phosphate species. If, on the other hand, ferric ion is produced homogeneously, each ferric ion, as soon as it is being formed, comes into contact and reacts with phosphate species. The better scavenging effect of homogeneously formed Fe (III) when compared to Fe (III) introduced directly is shown in Figure 3.

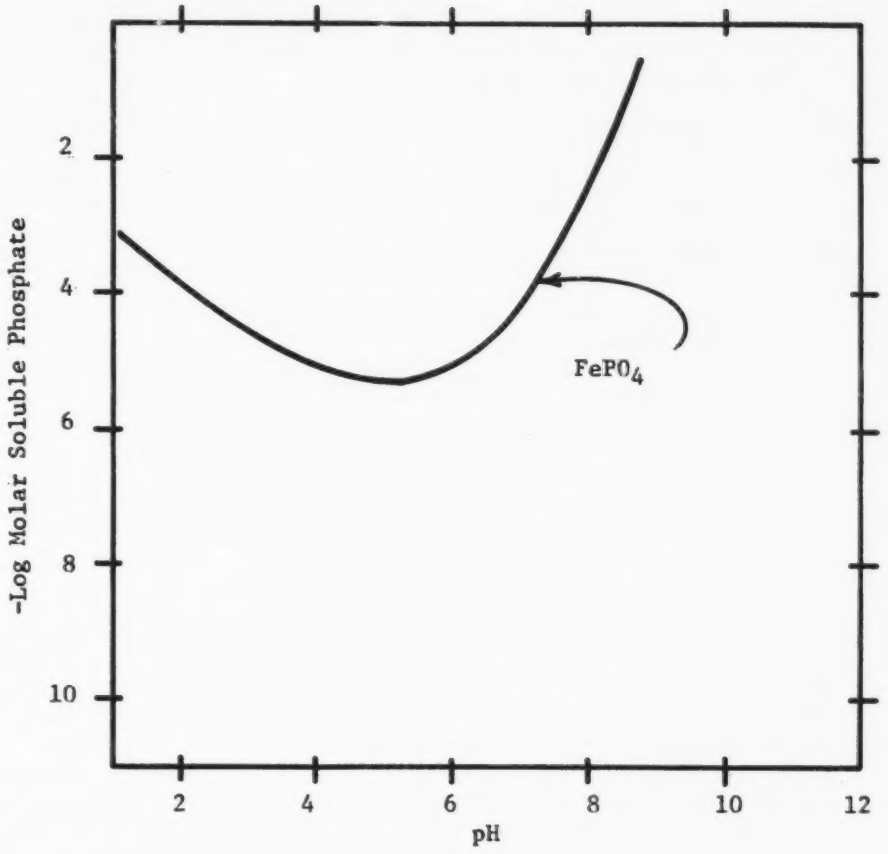

Figure 2. Solubility Diagram For Solid Phosphate Phase

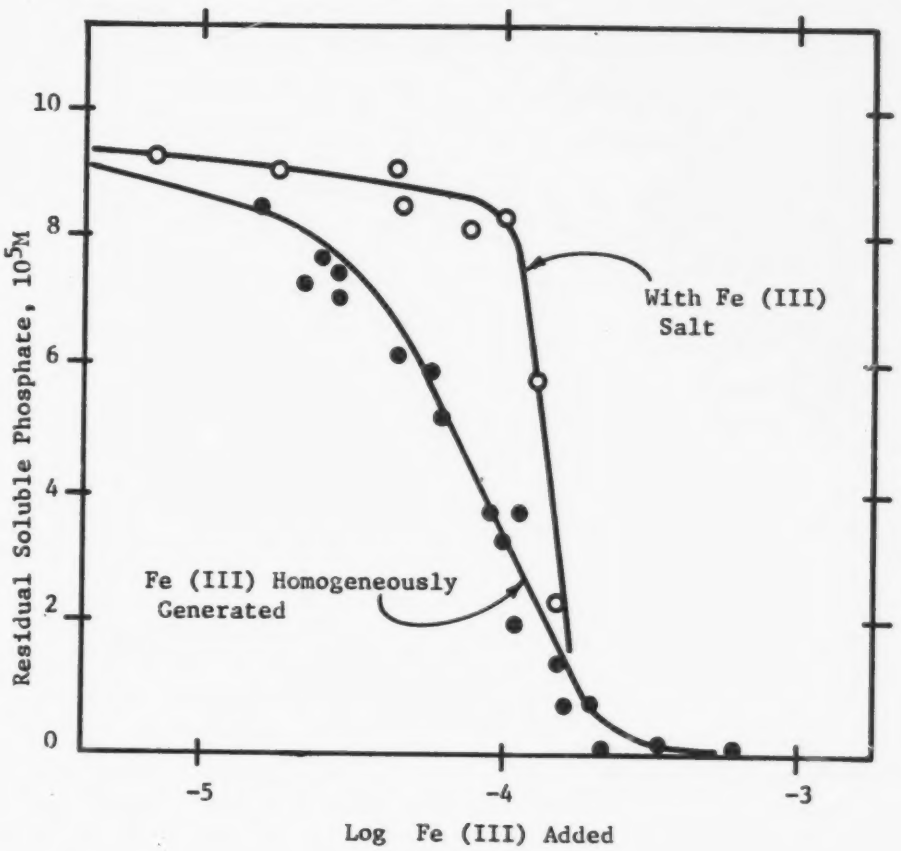

Figure 3. Precipitation of Phosphate By Fe (III)

SECTION V

SCOPE OF THIS STUDY

The subject study consisted of a literature review, laboratory experiments, and engineering analyses. The general literature review is given separately above and other previous published work is cited at appropriate places throughout this report.

Laboratory Investigation

The wastewater treatment processes studied were primary settling, activated sludge digestion, and anaerobic sludge digestion. The general approach was to compare the activity or effectiveness of acid-brine treated laboratory units with control (untreated) units with respect to COD removal, suspended solids removal, and phosphate removal. The broad question addressed was whether the unit process was degraded or enhanced by acid brine and neutralized (with lime) acid-brine.

Engineering Analyses

The general thrust of engineering analyses was economic. What are the estimated costs for brine production at the mine site; what are the costs of transporting brine via pipeline or by tankbarge, tanktruck, or railway tankcar; what is the value (if any) of acid-brine at a municipal wastewater treatment plant; what are the costs for lime or other basic salts for neutralizing acid-brine?

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SECTION VI

METHODS

For analyses of pH, acidity, alkalinity, iron, dissolved oxygen, BOD, COD, etc., Standard Methods (22) or simple modifications of standard methods were used. Raw sewage, primary sludge, digestor sludge, and primary effluent were obtained from the City of Norwich, Conn. sewage treatment plant. The Norwich sewer system is virtually completely combined stormwater and sanitary wastewater with some industrial wastewater including those from textile dying and finishing and food manufacturing. There is considerable day-to-day variation in the raw wastewater and in the quality of the primary effluent. The sewage is ordinarily faintly acid pH 5.5-6.5 with a total alkalinity of about 100 mg/L (as $CaCO_3$).

Artificial Acid Brine

The recipe for artificial acid brine (AAB) was devised to mimic a typical natural acid mine water concentrated about fifty-fold by a membrane process or any other suitable process (see Tables II, & III).

In order to simulate more ideally the composition of acid brines produced from natural acid mine drainage, all salts used should be the sulfates, because acid mine water is very low in other anions including chloride. The use of the magnesium and ferric chlorides, however, does not obviate the validity of any results obtained and reported here. The processes investigated are not sensitive anions over the range used in the present work.

Table II

Composition of Artificial Acid Brine

pH	2.0
acidity	5000 mg/L as $CaCO_3$
ferrous iron	1000 mg/L
ferric iron	1000 mg/L
magnesium	250 mg/L
aluminum	250 mg/L
manganese	100 mg/L
calcium sulfate	saturated

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The receipe used to achieve that composition is given in Table 3. The stock solution is labeled AAB-I.

Table III

Recipe for Artificial Acid Brine

Ferrous sulfate	$FeSO_4 \cdot 7H_2O$	5.0 gm
Manganous sulfate	$MnSO_4 \cdot H_2O$	0.3 gm
Potassium alum	$AlK(SO_4)_2 \cdot 12H_2O$	4.4 gm
Ferric chloride	$FeCl_3 \cdot 6H_2O$	4.8 gm
Magnesium chloride	$MgCl_2 \cdot 6H_2O$	2.1 gm

Make up to 1.0 liter with water saturated with calcium sulfate and adjust to pH 2.0 with sulfuric acid. The solubility of calcium sulfate dihydrate at room temperature is on the order of 3 grams per liter; a saturated solution has a pH of 6.3. Adding sulfuric acid to make the solution pH 2.0 does not increase the solubility because the sulfate added decreases the dissociation of the salt. The recipe above with sulfuric acid added to bring the pH to 2.0 has a titrated acidity of 7800 mg/L (as $CaCO_3$).

A second recipe (AAB-II) was used with ferrous iron (as the sulfate) added to make the total iron 10,000 mg/L. The second AAB formulation had a titration acidity of 23,000 mg/L (as $CaCO_3$). AAB stock solutions were stored under ambient conditions and no appreciable oxidation of ferrous iron occurs from contact with air because of the low pH. (2.0).

Experiments on Primary Settling

Using Standard Methods, total suspended matter was determined on various sewage treatment fractions by settling in an Imhoff cone and by membrane (0.45 microns porosity) filtration. For some purposes gravity filtration through coarse paper was used to obtain filtrates, a procedure which removes somewhat more suspended matter than primary settling. For obtaining decantate from laboratory anaerobic sludge digestors, centrifugation at 1800 rpm for five minutes was used. That speed corresponds to a relative acceleration value of about 600g. The centrifugation procedure produces a decant about equal in quality to gravity filtration through coarse paper. We have noted the type of separation procedure used in specific instances in the Discussion section.

Experiments on Activated Sludge Digestion

Laboratory units for activated sludge digestion (AS) were polyethlene battery jars of twenty-liters capacity containing about ten liters of mixed liquor. AS cultures were stirred with a one-inch disc impeller at about 1000 rpm and were aerated with a single tube with a capillary tip at the bottom of the culture. The aerators were set to deliver about 750 ml/min of air across a column depth of nineteen centimeters. The surface area of the cultures is 150 cm^2. These parameters combine to give an aeration rate of 50 L/m^2.min or 0.17 ft^3/ft^2.min. Dissolved oxygen measurements with a Yellow Springs Instrument Co. Model 54 dissolved oxygen meter indicated that dissolved oxygen in the AS cultures would fall to 40-60% of saturation following batch feeding and would rise to virtual saturation within one hour.

AS cultures were not thermostated; ambient temperatures varied between 60 and 85°F (16-29.5°C).

Suspended (settleable) solids levels in control AS cultures were maintained at about 40 ml/L, and in the AAB-fed cultures, at 190 ml/L. The average ratio of settleable solids volume by Imhoff cone (ml/L) to total suspended solids by membrane filter (mg dry/L) was 12.3 for control cultures and 10.8 for AAB-fed cultures. For 53 samples of control AS mixed liquor, the average total suspended solids was 492.5 mg dry/L and for seventeen samples of AAB-fed cultures the average was 2094.0 mg dry/L. These data are summarized in Table IV. The ratio of total suspended solids to settleable solids is not a valid measure of the dry weight per unit settled volume of the sludge because the total suspended solids also contains some so-called residual suspended solids or non-settleable suspended solids. Typical values of residual suspended solids--the total suspended solids by membrane filter of the Imhoff cone decantate--are 70 mg dry/L for control AS cultures and 190 mg dry/L for AAB-fed.

COD-Digestion Experiments

In a typical COD-digestion experiment, one or more control AS cultures would be fed a dose of primary effluent and the AAB-AS culture would be fed the same dose with twenty percent by volume of AAB. Samples of mixed liquor would be withdrawn periodically and settled in Imhoff cones, and the COD of the decantates would be determined. This was done day after day. A single experiment would involve taking the decantate COD before feeding, the decantate COD immediately after feeding, called the zero-time COD, and the decantate COD after two, four, six hours and 20-24 hours--the following day. In many experiments, only the 20-24 hour decantate COD was taken because of the difficulty in handling many COD analyses in a few hours time. In our experience, COD-digestion is virtually complete in four to ten hours. Corresponding BOD_5's were also taken in some instances. The BOD/COD relationship is discussed below. It was

promptly learned that raw AAB completely inhibited AS digestion, and from that time on all COD digestion experiments were done with AAB neutralized with lime (Pfizer-Nelco High Calcium lime containing 73.0% CaO and 0.5% MgO).

Table IV

Summary of Settleable Solids Volume and Mixed Liquor Total Suspended Solids for Activated Sludge Cultures

53 samples				17 samples			
Control Cultures				AAB-fed Cultures			
Settleable Solids (ml/L)		Total Suspended Solids (mg dry/L)		Settleable Solids (ml/L)		Total Suspended Solids (mg dry/L)	
Range	Ave.	Range	Ave.	Range	Ave.	Range	Ave.
20-70	40.1	200-900	492.5	150-260	193	1500-2400	2094.0
492.5/40.1 = 12.3 mg dry/ml				2094.0/193 = 10.85 mg dry/ml			

Correcting for non-settleable solids (see text)

492.5-60/40.1 = 10.8 mg dry/ml; 2094-190/193 = 9.8 mg dry/ml

Dosing Rate for AS Experiments

As has been mentioned, the Norwich sewer system is combined storm and sanitary. Thus during periods of heavy rains, the sewage becomes very dilute and at those times the primary effluent used as feed for AS cultures was augmented with a synthetic mixture of sucrose, potassium phosphate, and ammonium carbonate formulated to give a ratio of C:N:P of approximately 7:1:0.05 or 140:20:1. The recipe for SNP is given in Table V.

Table V

Composition of Stock Solution of SNP

Sucrose	250 gm/L
$(NH_4)_2\ CO_3.H_2O$	50 gm/L
KH_2PO_4	3.0 gm/L

SNP solution has a COD of about 250 mg/ml.

In a typical COD-digestion experiment four liters of mixed liquor would be drawn off and settled for sludge recovery and return (if necessary to maintain the design level), and for determination of the decantate COD before feeding. A four-liter batch of feedstock was prepared by mixing water, primary effluent of known COD, and SNP (if necessary) to bring the zero-time (after feeding) COD to about 400 mg/L. A typical calculation for the feed mixture is shown below.

$$COD_{zero} - t \tilde{=} 400 = 400 = \frac{4 \times COD_{feed} + COD_{before}}{10}$$

COD_{before} was typically about 60 for control AS and 120 for AAB-fed. Thus for a nominal value of 100, COD_{feed} would be 850 mg/L. If primary effluent were higher than that, it would be diluted with water; if lower, SNP would be added.

Anaerobic Sludge Digestion

Two anaerobic sludge digestors for four-liters capacity were charged with 400 ml heavy primary sludge plus 2500 ml water. Thereafter one was maintained on control activated sludge and the other on AAB-fed activated sludge. The digestors were kept closed and stirred with a magnetic stirring bar. The digestors were not heated; the ambient temperature varied between 65 and 75°F (18.5 and 24°C). The head-space in the digestors was 900 ml. Every morning the anaerobic cultures were removed from the stirring motor and permitted to settle. A 100-ml portion of decant was removed for analyses and 100 ml of settled activated sludge was added to restore the original volume. Decant samples were analyzed for pH, iron, COD, occasionally BOD, and total phosphorus. Occasionally small samples of mixed liquor were withdrawn for total suspended solids determinations to follow the course of sludge accumulation and/or digestion. Toward the end of the period of experiment, it was deemed expedient to obtain decantate by centrifugation.

Activated Sludge Digestion of Anaerobic Sludge Digestion Decantate

Conventionally, digested sludge is either drawn off and dried on sand beds for land-fill disposal or it is dewatered on a vacuum drum filter. In the latter case the filtrate, which is very high in BOD and COD is recycled through the plant. In order to determine the treatability of anaerobic sludge digestion decantate, we centrifuged the contents of our two digestors. The decantate from the control digestor had a COD of more than 4000; the decant from the sludge digestor fed iron-rich activated sludge had a very low COD--on the order of 100. The former (control) decantate was passed through the AAB-fed AS digestor without added AAB, and the latter (iron-rich) decantate was passed through a control AS digestor augmented with SNP synthetic feed-stock to a COD level equal to our conventional batch

feed. The purpose of the latter test was merely to determine whether the iron-rich anaerobic decantate was toxic to AS. As discussed later, the decantate proved to be nontoxic.

SECTION VII

RESULTS AND DISCUSSION

Experiments on Primary Settling

Experiments on sludge settling were carried out in Imhoff cones. The results of a preliminary experiment on the effects of AAB, lime, and AAB plus lime are shown in Table VI.

On the occasion of the preliminary experiment raw Norwich sewage contained only a small amount of settleable solids (this is frequently the case). Lime alone improves settleability markedly, if sufficient lime is added to bring the pH to 10.5. That effect may be due in part to precipitation of sesquioxides. It is not shown in the Table (VI) but the quantity of acid required to neutralize the lime treated sewage from pH 10.5 to pH 8.4 (as if for stream discharge from primary sewage treatment only) is equivalent to 50 mg/l (as $CaCO_3$). Coincidentally, that is equal to 50 mg H_2SO_4/L. AAB alone enhances solids settling appreciably, albeit this response is much more variable than with lime alone. AAB alone causes some coagulation of suspended matter but the clots are bulky and sludge volume shown in Table VI is somewhat misleading. Neutralizing the AAB-sewage mixture is equivalent to adding AAB plus lime, in which case a hydrous iron oxide floc forms, which scavenges colloid and other particles as it settles. The addition of AAB plus lime produces a copious sludge, which settles very rapidly (a few minutes), and produces a clear effluent, albeit a pale yellow-colored one.

Another preliminary experiment is shown in Table VII.

The data of Table VII confirm in a general way the results of earlier preliminary experiments. The improvement in clarity of the supernatant from AAB plus lime is especially noteworthy. The addition of AAB at a level higher than 10% AAB-I vol/vol as shown in sample #6 does not improve decantate clarity; AAB-II at 5% vol/vol is equivalent in its iron content to 25% AAB-I. In these experiments turbidity was measured with a Klett-Summerson industrial model colorimeter using a #42 blue filter. The decantate from AAB/Lime treated samples is very clear but it does have some yellow color; except for highly colored solutions, however, the error is not significant. In order to check the sludge volume due to iron precipitates themselves and to determine the apparent turbidity of the decantate due to AAB itself, a sample of AAB 10% vol/vol in water was neutralized with lime to pH 7.6 and the sample was settled in an Imhoff cone in the usual way. That sample is shown as sample #7 in Table VII. The sludge volume of 250 ml, higher than that of sample #5 (180 ml), indicates either that precipitation of iron hydrous oxide is inhibited somewhat by substances in sewage or that the solids in AAB/lime treated sewage settle more densely than

TABLE VI

Preliminary Experiment on AAB and Lime Effects on Primary Settling

Sample #	Treatment	pH	Volume of Sludge Settled (ml)	Clarity of Supernatant
1	none	5.7	4.0	poor
2	none	5.7	5.0	poor
2A	none	6.0	2.0	poor
3	Lime	9.0	12.0	poor
3A	Lime (200 mg/L)	9.7	6.0	fair
4	Lime	7.0	6.0	poor
5	AAB-I + Lime (10% vol/vol)*	7.1	80.0	good
6	AAB-I (10% vol/vol)	3.0	40.0	fair
6A	AAB-I (10% vol/vol)	3.0	12.0	fair
7	Lime (250 mg/L)	10.5	30.0	fair

* AAB-I + Lime (10% vol/vol) means the part lime neutralized AAB-I to nine parts sewage.

TABLE VII

Further Preliminary Experiments on
Primary Settling

Sample #	Treatment	pH	Volume of Sludge Settled (ml)	Relative Turbidity of Supernatant
1	none	6.8	12	225
2	Lime (100 mg/L)	7.5	15	200
3	AAB-I (10% vol/vol)	2.4	23	190
4	AAB-II (5% vol/vol)	2.8	32	225
5	AAB-I + Lime (10% vol/vol, lime to pH 6.0)	6.0	180	35
6	AAB-II + Lime (5% vol/vol, lime to pH 6.0)	6.0	190	45
7	AAB-I + Lime (10% vol/vol in water)	7.6	250	8

the hydrous iron oxide in lime-neutralized AAB. Judging from the appearance of the settled hydrous iron oxide in the latter case, we prefer the interpretation that the sewage-solids/hydrous-iron-oxide mixed solids are denser. The turbidity of the decantate from sample #7 was 8 units; thus, the turbidity from suspended solids of samples #5 and #6 can be considered to be slightly lower than the measured turbidities shown in Table VII. For comparative purposes, a kaolin suspension prepared according to Standard Methods gives a Klett turbidity of 4.5 units per mg kaolin/L.

The results of a third preliminary experiment on primary settling are shown in Table VIII.

The results confirm earlier experiments. Especially noteworthy are samples #5 and #6 which show that amounts of lime-neutralized AAB in excess of 10% AAB-I do not give any further improved clarification of sewage, and also sample #4, which shows that lime in a quantity of sufficient to raise the pH of the Norwich sewage to pH 9.0 significantly improves primary settling. In other trials with lime alone, we observed that settled sludge volume was approximately doubled by lime treatment to pH 10 or slightly higher.

The results of a definitive experiment, in which COD analyses of primary settling decantate were carried out, are given in Table IX.

Unlike earlier experiments, this experiment showed good clarification from the highest level of lime-neutralized AAB tested (50% AAB-I equivalent to a total iron concentration of 1000 mg/l in the AAB/sewage mixture). Of course, something less than half of the clarification is due to the simple dilution effect. It should be noted that the turbidity units are given in terms of the kaolin equivalent in mg/l; for comparison with earlier reported turbidities in Klett optical density units multiply by 4.5. Thus the sewage used in this experiment had a Klett turbidity of 330 units in comparison to 160 and 225 units in earlier experiments. On the other hand the sewage had virtually no settleable solids as shown by sample #1.

The COD removal by 10% neutralized AAB-I (sample #4) was 23%, and for 50% neutralized AAB-I (sample #6), nil. At the lower concentration, neutralized acid brine can remove some suspended and soluble COD not removed by ordinary primary settling.

In order to determine the effect of pH on the decantate clarity and COD-removal in AAB-treated sewage, an experiment using 10% vol/vol AAB-I was run. The results of the experiment are given in Table X.

From the data it is clear that the optimum lies between 6 and 8. That conclusion agrees with Packham's (23) results on water clarification using alum. Packham determined the amount of alum needed to remove 50% of various colloidal suspensions (kaolin, other clays, calcite, and quartz) as a function of pH. The minimum quantity of alum for 50% removal

TABLE VIII

Effect of AMD and Lime on Primary Settling

Sample #	Treatment	pH	Sludge Volume (ml)	Turbidity of Decantate
8	none	6.0	7.5	160
1	AMD-I (10% vol/vol)	2.8	12	90
2	AMD-I (50% vol/vol)	2.0	1	135
3	AMD-II (10% vol/vol)	2.6	7.5	160
4	Lime	9.0	8	90
5	AMD-I + Lime (10% vol/vol; Lime to pH 7)	7.0	200	65
6	AMD-I + Lime (50% vol/vol; Lime to pH 7)	7.0	350	95
7	AMD-II + Lime (10% vol/vol; Lime to pH 7)	7.0	400	75

TABLE IX

Effect of AAB and Lime on Primary
Settling--Decantate COD

Sample #	Treatment	pH	Settled Sludge Volume (ml)	COD* mg/L	Turbidity (Equiv. Kaolin Suspension)
1	none	7.1	< 1.0	945	73
3	Lime alone (250 mg/L)	10.0	10	854	63
2	AAB-I alone (10% vol/vol)	3.0	12	900	105
4	AAB-I + Lime (10% vol/vol; 1100 mg Lime/L)	7.0	230	735	13
5	AAB-I alone (50% vol/vol)	2.4	< 1.0	1000	86
6	AAB-I + Lime (50% vol/vol; 5650 mg Lime/L)	6.8	400	1000	21

* Corrected for dilution and COD of ferrous iron added

TABLE X

Effect of 10% AMD-I on Primary Settling & The pH Effect on the System

	Experiment					
	1	2	3	4	5	6
pH of decant	7.0	2.9	4.3	5.6	6.2	8.3
Lime requirement (mg/L)	0	0	310	610	1000	1250
Settled volume (ml)	0	24	120	172	172	230
Turbidity (mg/L)	75	100	45	13	17	8
Decantate COD (mg/L)	875	644	550	530	494	494
COD removal (%)	---	25	35	40	45	45

of all the colloids fell between 6.5 and 7.5. Morgan and Stumm (24) suggested that hydrous iron oxide suspended particles bind anions and colloids optimally at a pH range of 5.0 to 8.0.

To determine more precisely the effect of concentration of neutralized AAB on primary settling, an experiment was conducted using AAB-I at 5, 10, and 25% levels, and AAB-II at 5 and 10%. To obviate the necessity for making corrections on COD analyses, COD measurements were made on the gross mixtures (before settling) and on the decantates after settling. The results of the experiment are given in Table XI.

On the assumption that acid brines would only be disposed of in municipal wastewater treatment plants with secondary or higher grade treatment, the turbidity data is only of interest as a very rough measure of removal of suspended solids. Based on corrected turbidity measurements, the optimum level of AAB is AAB-I 10%; the corresponding level of AAB-II is 2%. In terms of COD removal, the highest AAB levels tested gave the best results. It should be stressed, however, that higher levels of AAB require larger amounts of lime for neutralization. Furthermore, the sludge volume to be disposed of, mostly hydrous iron oxides, is considerably greater at the higher AAB levels. For example, for 25% AAB-I or 50% AAB-I, the settled sludge volumes are 50% and 45% of the volume of raw sewage treated, respectively.

The general conclusions drawn from the above experiments are that primary settling is improved by the addition of AAB at a level as high as 10% vol/vol neutralized with lime to a pH in the range of 6.0 to 8.0, that the lower end of the pH range calls for less lime, and that primary settling is not impaired by AAB in the range 10-15% even without neutralization. As will be shown later in this report, neutralization of acid in added AAB is necessary for proper functioning of activated sludge. The option of neutralizing before or after primary settling is however open to the operator. If primary sludge is combined with settled activated sludge for disposal, however, the option is academic.

Experiments on Activated Sludge Digestion

Activated sludge cultures (AS) were operated on a daily batch basis on weekdays during October, November, and December. A series of experiments on acid (AAB) shocking of AS cultures was carried out to determine the safe interval between adding AAB and neutralizing to the physiological range of pH. It should be noted that the alkalinity of the primary effluents we used was only about 100 mg/l as $CaCO_3$ which is equivalent to only 13 ml of AAB-I stock solution. If more than that quantity of AAB is added to primary effluent, the pH drops below the physiological range. Other experiments were carried out to compare AS digestion in control cultures with that of a culture fed lime-neutralized AAB. A third series of experiments was done to determine the AS digestibility of decantate from anaerobic sludge digestors.

TABLE XI

Effect of Concentration of AAB on Primary Settling

Sample #	Treatment	pH	Lime Required (mg/L)	Turbidity Kaolin Equivalent (mg/L)		COD			Settled Sludge Vol. (ml)
				Uncorr.	Corr. for Color	Before Settling (mg/L)	Decantate (mg/L)	% Removal	
1	None	6.5	---	90	90	1550	1440	7	4
2	AAB-I (5% vol/vol)	7.2	300	325	44	1550	1135	27	40
3	AAB-I (10% vol/vol)	7.2	1000	89	27	1550	1025	34	170
4	AAB-I (25% vol/vol)	7.6	2000	74	59	1760	950	51	380
5	AAB-II (5% vol/vol)	7.2	1000	205	163	1480	1010	32	280
6	AAB-II (10% vol/vol)	7.2	2500	280	214	1580	920	42	400

Experiments on Acid Shocking

The results of acid shocking experiments are given in Table XII. The experiment shown was done at low loading; but it is obvious that exposure to acid for only one-half hour does not seriously impair digestion. Exposures for one hour or longer does inhibit digestion. In a second experiment a culture was exposed to acid for 24 hours and then neutralized and fed a portion of strong waste sufficient to bring the initial COD to 1000 mg/l. Both the control and the acid-exposed AS culture gave a 24-hour Δ COD of about 250 mg/l or about 25% COD removal in 24 hours. A third experiment at low loading was carried out on a culture exposed to acid for 24 hours (pH 3.2). After the exposure, the culture was neutralized and fed along with a control. The results are given below. Although digestion is obviously slowed down for 16 hours, after 24 hours a comparable amount of digestion is obtained.

	Control		Acid-Exposed	
	COD	% removal	COD	% removal
initial	185		148	
16 hrs.	73	60	129	13
18 hrs.	92		111	
24 hrs.	75	60	75	50

In a fourth experiment, COD digestion was followed for the first two hours after neutralizing and feeding an AS culture exposed to acid for 24 hours. The results are given below:

	Control		Acid-Exposed	
	COD	% removal	COD	% removal
initial	310		292	
20 min.	256		292	
60 min.	220		256	
120 min.	183	40	256	12

Thus, COD digestion begins within an hour of neutralizing and feeding but the inhibition is quite marked.

The general conclusions to be drawn from the above experiments are that AS cultures can be exposed to AAB at concentrations sufficient to reduce pH to below 3 for one-half hour without significantly affecting

TABLE XII

Acid Shocking of Activated Sludge Cultures

	Exposed to AAB			Control
	Time exposed before neutralizing			
	1/2 hour	1 hour	4 hours	
	COD			
initial	115	115	115	133
2 hr.	73	75	91	49
4 hr.	75	73	85	36
6 hr.	36	85	--	29
24 hr.	--	67	75	--

the COD digestion capability. Longer exposures damage the digestion capability, but activity recovers after neutralization. The time required for recovery depends upon the time of exposure and on the loading, which introduces new active microbes along with digestible organic matter. Even with an exposure to acid of 24 hours and with a low loading following neutralization, recovery is virtually complete in 24 hours. Even before recovery, a reasonably clear effluent with some COD removed can be produced in the damaged culture because of the improvement in suspended solids removal due to hydrous iron oxide.

COD Digestion by Activated Sludge

A comparison between the day-to-day performance of control AS cultures and a culture fed neutralized AAB is given in Table XIII. Table XIII shows the initial COD's, the COD after 24 hours aeration, and the % removal of COD in the two types of AS cultures. Some typical COD-depletion curves are given in a later section (COD digestion by AS on anaerobic sludge digestion decantate), but for present purposes it is sufficient to say that 85-90% of the 24-hour digestion occurs in the first ten hours. From the data it is clear that the performance of the AAB-fed culture is about the same as that of the control in terms of daily COD removal. The lower COD removal (average 64.3%) in the AAB-fed culture in comparison to the control (average 70.8%) may be due in part to the fact that the AAB-fed culture was loaded in the average at a rate about 6% lower than the controls, without regard to the solids levels in the cultures. The settleable solids level in the AAB-fed culture was maintained at about 190 ml/L as compared to about 40 ml/L in the controls, but the greatest part of the solids in the AAB-fed culture was hydrous iron oxide (and other hydrous sesquioxides). Judging from mixed-liquor COD and BOD analyses the organic solids contents of both types of AS cultures were about equal, at around 500 mg dry solids/L.

We note a rough trend in the data on COD removal in which the performance in the second half of the period is poorer than in the first half while just the opposite seems to be the case in controls. In the latter case, one can attribute the trend to adaptation to the substrate; in the former case we would attribute it to an increased turbidity in the one-hour decantates. The turbidity seemed to be due to very small coccoid bacteria with a thin rind of iron oxide, but we would not press that point too far. With longer settling times, e.g. four hours, the AAB-fed AS cultures produces a remarkably clear decantate. Another important characteristic of the AAB-fed activated sludge is its filterability. Ordinary activated sludge clogs a laboratory vacuum filter (paper or membrane) in a matter of seconds, whereas the AAB-fed AS filters rapidly through a thick pad of sludge. The same can be said of the anaerobically digested sludges.

COD/BOD Relationship

In order to translate treatment effectiveness measured by COD

TABLE XIII

Effect of Neutralized AAB on Activated Sludge Digestion

	Control				AAB			
	COD_o	COD_{24}	ΔCOD	% removal	COD_o	COD_{24}	ΔCOD	% removal
Oct. 13	475	110	365	77	335	170	165	49
Oct. 16	380	190	190	50	226	100	126	56
Oct. 19	340	130	210	62	170	55	115	68
Oct. 28	228	91	137	60	177	18	159	90
Oct. 30	446	102	344	77	464	102	362	78
Nov. 2	273	86	127	46	213	137	76	36
Nov. 4	358	68	290	83	307	51	256	83
Nov. 5	415	135	280	68	364	51	313	86
Nov. 6	334	140	194	58	296	70	226	76
Nov. 10	242	46	196	81	284	120	164	58
Nov. 12	309	101	208	67	329	134	195	59
Nov. 13	405	50	355	88	373	120	253	67
Nov. 17	486	50	436	89	465	175	290	62
Nov. 18	300	56	244	81	275	93	182	66
Nov. 19	209	37	172	82	190	113	77	41
Nov. 23	300	38	262	87	280	91	189	68
Dec. 9	366	51	222	61	315	144	171	54
Dec. 14	1265	--	774	61	925	---	521	56
Dec. 16	495	84	329	67	401	124	277	69
Dec. 21	---	--	----	--	357	133	224	63
		Average		70.8				64.3

changes into BOD terms, both waste-strength parameters were measured on various waste treatment fractions--primary effluent, AS mixed liquor, AS decantate, and anaerobic sludge digestor decantate. The results of the analyses are given in Table XIV. As can be seen in the data, the Norwich primary effluent has a lower COD than BOD, the average COD:BOD ratio being 0.72. In oxidation of organic matter by acid chromate, the oxidation proceeds only to the stage of low molecular weight organic acids; in other words, low molecular weight organic acids are refractory in the COD analysis. The Norwich sewage is almost always slightly acid and has a sour or ester-like odor. Control AS mixed liquor shows an average COD:BOD ratio of 1.46, which is typical of a general mixture of biological materials. Cell walls and cellulosic matter are nearly completely oxidized by acid chromate, but only incompletely in a 5-day BOD incubation. The COD:BOD ratio is higher in the AAB-fed mixed liquor (1.93) indicating more biorefractory materials in the sludge. The decantates from AS cultures have even higher COD:BOD ratios, a reflection of the fact that biological sorption and oxidation of substrate has taken place in the AS cultures. Decantate from the anaerobic sludge digestor fed control sludge has a COD:BOD ratio of about 1 and even more noteworthy a very high COD and BOD. The anaerobic sludge digestor fed iron-rich sludge (from the AAB-fed AS culture) had very low COD and BOD in comparison. The ratio in this last case is of no particular significance.

We have discussed AS digestion in terms of COD thus far. Because of the COD:BOD ratios, the performance of AS cultures in BOD terms can be shown to be markedly better, as follows.

$$\% \text{ COD removal} = \frac{COD_0 - COD_{24}}{COD_0} \times 100;$$

in a typical case:

$$75\% = \frac{400 - 100}{400} \times 100$$

With our typical batch feeding regime where four liters of primary effluent is fed to a starved AS culture with a final volume of ten liters,

$$COD_0 = \frac{\text{AS decantate COD} \times 6 + \text{Primary Effluent COD} \times 4}{10}$$

in a typical case:

$$400 = \frac{100 \times 6 + 850 \times 4}{10}$$

Using the average COD:BOD ratios from Table XIII to convert COD to BOD, one gets:

$$BOD_0 = \frac{(100/1.9)\ 6 + (850/0.72)4}{10} = \frac{315 + 4700}{10} = 502$$

and

$$\% \text{ BOD removal} = \frac{502 - 100/1.9}{502} = 90\%$$

TABLE XIV

COD:BOD Relationship of Various Waste-Treatment Fractions

WASTE FRACTION		COD	BOD		COD:BOD
Primary effluent		910	1030		0.88
		1010	1690		0.60
		755	1380		0.55
		1590	1900		0.83
				Ave.	0.72
Activated Sludge Mixed liquor	Control	750	520		1.45
		750	620		1.20
		650	470		1.40
		770	350		2.20
		800	770		1.05
				Ave.	1.46
	AAB-Fed	725	380		1.90
		855	520		1.65
		810	360		2.25
				Ave.	1.93
Activated Sludge Decantate	Control	90	55		1.65
		145	70		2.07
		165	85		1.95
		135	55		2.45
		150	90		1.65
		104	60		1.73
				Ave.	1.92
	AAB-Fed	144	35		4.12
		710	800		0.90
		102	52		1.96
		95	90		1.05
		173	52		3.33
				Ave.	2.44
Anaerobic Sludge Digestor Decantate	Control	3990	3690		1.10
		4150	3860		1.10
		4300	5780		0.75
				Ave.	0.98
	Iron-rich	218	210		1.05
		165	100		1.65
		160	90		1.75
				Ave.	1.48

In the case of AAB-fed AS, with a typical effectiveness of 65% COD removal and with an AS-decantate COD:BOD ratio of 2.4, the same calculation shows removal to be also 90%.

Activated Sludge Digestion of Anaerobic Sludge Digestion Decantate

After anaerobic sludge digestors (SD) had operated for about a month, the whole volumes of the decantates were collected and passed through activated sludge to determine toxicity (if any) and digestibility. As is discussed in a later section, and as is shown in Table XIV, the decantate from the SD fed iron-rich sludge had a low COD (175) whereas the SD fed control sludge had a decantate with about 4000 mg/l of COD. The iron-rich SD decantate was augmented with SNP and fed to a control AS culture. The decantate from the SD fed control sludge was suitably diluted and fed to the AAB AS culture. The results are given in Table XV and Figure 4.

From the results shown, it is obvious that iron-rich anaerobic decantate is not toxic to ordinary activated sludge, and AAB-fed AS can handle control anaerobic decantate about as well as it digests ordinary primary effluent. Other qualities of the anaerobic decantates are discussed later.

Tertiary Treatment

Activated charcoal adsorption has become a major tertiary treatment method. Zuckerman and Molof (25) recently discussed alkaline hydrolysis (with lime at pH 11.5) as a preliminary step to adsorption and they concluded that activated sludge secondary treatment adds nothing to the over-all effectiveness of treatment when hydrolysis/adsorption is used for tertiary treatment. In alkaline hydrolysis treatment it is necessary to readjust pH to the neutral range with carbon dioxide or strong mineral acid. Although hydrolysis/adsorption treatment is still in the pilot plant stage of development, it is of interest to consider how acid brine disposal could affect the method. Obviously acid brine could be used to adjust pH following alkaline hydrolysis, and the acid would itself be neutralized in the process. The hydrous iron oxide precipitate would also no doubt assist in the flocculation of unhydrolyzed colloidal organic particles and molecules. On the other hand, the unsettleable hydrous iron oxide might have an adverse effect on adsorbtion or regeneration of activated charcoal.

Ozone has also been promoted for destruction of refractory organic matter and for disinfection. Precise pH control and adequate buffering are very important to the effectiveness of ozonation (26). For the integrity of activated sludge, it is necessary to neutralize acid brine, as has been discussed. The neutralization process can be carried to any pH between 2.0 and 11.5 and the resultant mixture is well buffered. Copper oxide has been shown to be an important heterogeneous catalyst in ozonation, but the role of other metal oxide particles (including iron) is problematical. The impact of lime-neutralized brine on ozonation is a prime subject for future research.

TABLE XV

COD-Depletion Experiment on Anaerobic
Sludge Digestor Decantates

AAB-AS			Control-AS		
Fed Control Decantate			Fed Iron-Rich Decantate		
Time (hrs)	COD (mg/L)	% removal	Time (hrs)	COD (mg/L)	% removal
0	416		0	547	
2	340		2	416	
4	265		4	360	
6	234	43	6	252	54
24	162	61	24	108	80

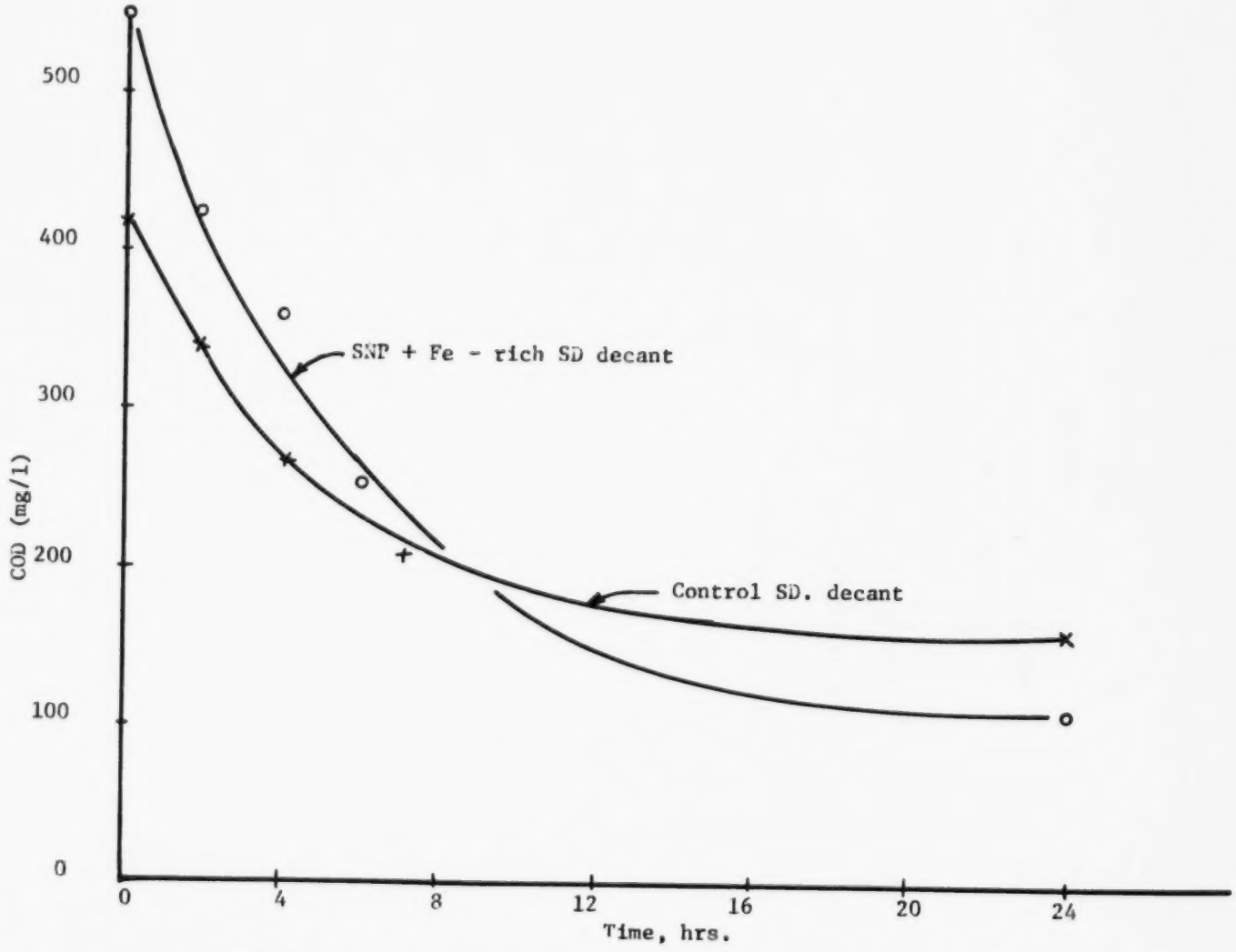


Figure 4. Activated Sludge Digestion of Anaerobic Decantate

TABLE XVI

Phosphate Removal from Primary Effluent
by Lime and AAB Treatment

Portion	Treatment	Total Phosphorus (mg P/L)
1	None pH = 5.8	8.50
2	Membrane filter (0.45 micron)	5.83
3	Add lime to pH 8.5 decant	3.00
4	Add lime to pH 9.7 decant	1.45
5	Add AAB-I 20% vol/vol Add lime to pH 7.7 Membrane filter	zero*
6	As portion 5, but decant	trace
7	As portion 5, but aerate 15 min. before decant	trace

* In our method of analysis, zero P means much less than 0.020 mg P/L; trace means approximately 0.015 mg P/L.

Phosphate Removal

Phosphate removal from primary effluent by lime and by AAB plus lime was studies on a batch of effluent containing 8.5 mg total P/L and 5.83 mg soluble P/L. Several portions of the effluent were treated in various ways and the membrane filtrates or decantates were acid digested and analyzed for P by the standard molybdate-blue method with the following results (Table XVI). From the results it is apparent that treatment with AAB plus lime gives virtually 100% removal of phosphate in the filtrate or decantate. In actual plant practice, where alum, lime, iron salts, or combinations of them are used for phosphate removal, only slightly more than stoichiometric quantities are used because of cost, and typically only about 90% (or less) removal of phosphate is accomplished. For efficient phosphorus removal, according to Wuhrmann (20), the stoichiometric amount of iron (Fe:P equal to 1.8) has to be supplemented with at least 10 mg Fe/l for hydroxide floc formation. Wuhrmann showed the lime sufficient to raise the pH to 8.8 can be substituted for the excess iron, in which case sludge quantity and volume will be much reduced and the sludge produced has better handling properties. If the emphasis is on acid brine disposal, those points are mott.

The actual amounts of Ca and Fe contained in tests 5, 6, and 7 are shown in Table XVII along with the stoichiometric amounts in relation to phosphorus based on the empirical formula of the simplest iron phosphate and calcium phosphate salts. In addition to the iron and calcium, test protions 5, 6, and 7 contained 25 mg Al/1.

TABLE XVII

Fe, Ca, and Al Contents of Test Samples for Phosphate Removal

	Actual Amount (mg/L)	Stoichiometric Amount (mg/L)	Factor of Excess
P	8.5	----	----
Fe	200	15.2	13.3x
Ca	325	16.6	19.6x
Al	25	7.4	3.4x

Analyses for nitrogen fractions were not included in the protocol for phosphate removal test, but some information is available from the literature. Neil (27) used a combination of alum (94 ppm = 8.5 mg Al/L) and activated silica (3.4 ppm) for raw sewage treatment and he reported removal of 98% soluble phosphate; Kjeldahl nitrogen was reduced

by 35%. Rohlich (28) observed that 200 ppm of alum (18 mg Al/L) added to the effluent of the Madison, Wis. Nine Springs Sewage Treatment Plant reduced phosphate to 0.06 mg P/L (from an initial value in range 5-10 mg P/L), and the treatment effected a 68% removal or organic nitrogen compounds. Rohlich found no removal or inorganic nitrogen compounds. There is no reason to expect sorption and/or precipitation of ammonia or nitrate by lime, alum, or iron salts. Rohlich and colleagues (29) later reported 60% removal or organic nitrogen (from secondary effluent) by flocculation with 250 mg alum/L. In the same tests 25% removal of nitrate and nitrite was found but no removal of ammonia nitrogen. The possibility of nitrate reduction and/or denitrification by ferrous iron is discussed later. Rand and Nemerow (30) reported preliminary results of chemical flocculation studies at the Metropolitan Syracuse Treatment Plant using 5 ppm $Fe_2(SO_4)_3$ and 30 ppm lime. For three runs, they observed 48, 64, and 80% phosphate removal. Kjeldahl nitrogen <u>increased</u> in two of the three runs, which was attributed to "sampling procedures". On the single run in which Kjeldahl nitrogen was reduced, 22% removal was found. Thus it is reasonable to conclude that chemical coagulation of sewage fractions can remove a significant amount of nitrogen.

<u>Biological Nitrification and Denitrification</u>

It was hoped in the present project to study the effect of AAB on biological nitrification and denitrification, but we were unable to produce an adapted sludge culture until the last few days of the period devoted to experimental work. A description of the management and behavior of the nitrifying sludge culture follows.

--Recipe for feed stock solution (SGP) for nitrifying Sludge cultures --

Sucrose	15.0 g/L
Gelatin	11.7 g/L (~7% N)
KH_2PO_4	0.8 g/L

The mixture has a pH of 6.2

-- Ammonium sulfate stock solution (to contain 10 mg N/ml).

$(NH_4)_2SO_4$	47 g/L

--Soil extract is made from rough turf growing on a fertile sandy loam low in calcium. Ten grams of air-dried soil is treated with 100 ml hot water and the mixture is filtered through coarse paper.

A typical daily routine would be to feed 15 ml SGP, 10 ml soil extract (for trace elements) and 2 ml ammonium sulfate (20 mg N). Sludge solids in the culture were maintained at 1400-1600 mg/L by wasting or returning settled sludge.

Data on a typical run are given below.

Time	Nitrate in decantate NO_3 . N (mg/L)	
Before feeding	18	pH 5.7
20 min. after feeding	16	
40 min. after feeding	4.5	
60 min. after feeding	4.0	
150 min. after feeding	19	
24 hrs. after feeding	20	pH 5.5

On this regime, the nitrate nitrogen content before feeding will remain in the neighborhood of 20 mg N/L. The diminution of nitrate after feeding is problematical but we would attribute it to binding or sorption of nitrate to gelatin and sorption of gelatin by sludge cells. Metabolic uptake of nitrate is a simpler explanation, but we do not believe that would occur in the presence of 20 mg NH_3.N/L, and under a high rate of aeration. Biological nitrogen removal has been comprehensively reviewed by Wuhrmann (20) and also by Balakrishnan and Eckenfelder (31). According to Wuhrmann the nitrogen status of sewage fractions is typically as shown in Table XVIII.

TABLE XVIII

Nitrogen Status of Sewage Fractions (20)

	Organic N	NH_3-N	NO_3/NO_2-N
Primary effluent	40-45%	50-60%	0-5%
After biological	$<$20%	10-60%	20-80%

Over-all proper biological treatment removes about 50% of total nitrogen from primary effluent. The proportions of ammonia-N and nitrate/nitrite-N in the effluent from biological treatment varies over wide limits depending upon operating conditions in the plant. The general scheme for biological nitrogen removal involves digestion of nitrogenous organic matter by a variety of aerobic heterotrophic

microbes, conversion of ammonia to nitrate by Nitrosomonas spp. and Nitrobacter spp. (nitrification) and conversion of nitrate to molecular nitrogen (or to N_2O according to Wuhrmann) under anaerobic conditions by a variety of "nitrate-respiring" bacteria- Nitrate can also be feduced to ammonia by a variety of microbes, and culture conditions with regard to detention time and loading rate in the aeration stage must be controlled in order to favor denitrification over mere nitrate/nitrite reduction (to ammonia) under anaerobiosis.

Nitrification (the oxidation of ammonia to nitrate) is a two-step process effected by two microbial groups:

Nitrosomonas spp.

1) $NH_3 + 3/2\ O_2 \longrightarrow NO_2^- + H_2O + H+$

nitrite

Nitrobacter spp.

2) $NO_2^- + 1/2 O_2 \longrightarrow NO_3^-$

nitrate

The growth rate of both those groups of organisms is low in comparison to ordinary heterotrophic bacteria and their growth is more diminished by low temperatures. Thus in continuous AS culture, in which both decantate and excess sludge are continuously being harvested, the nitrifying microbes can easily be washed out of the culture. In batch culture, the experimentor has more freedom to alter compositon of the feed, feed dosing, return sludge, etc. but in the in the long run, the problem is the same, maintaining enough of the active species to handle the dosing of ammonia. Over-all, nitrification is dependent upon conditions of operation which minimize excess sludge production. The critical oxygen tension for nitrification is lower than formerly thought. A concentration as low as 1.0-1.5 mg O_2/L is adequate.

As we mentioned, denitrification requires anaerobic conditions; this condition can be achieved simply by holding sludge without air for a time. After a period of aeration and limited feeding sufficient to induce nitrification, exogenous substrate has been used up but sufficient endogenous substrate remains to maintain the nitrate respiration of the sludge until all the nitrate is used up. It is not necessary to add raw sewage or other exogenous sources of hydrogen donor substances if endogenous reserves are present in amounts equal to the nitrate/nitrite. In fact one gets the impression that exogenous substrate may promote nitrate reduction as opposed to denitrification.

Biological nitrogen removal can thus be seen to depend upon a number of parameters, some hydraulic and some biological or chemical. In the disposal of acid brines through municipal waste treatment plants, nitrogen removal could be profoundly affected; for example, high ferric iron concentrations may favor nitrifying species over ordinary heterotrophs, ferrous iron can reduce the time needed for nitrifying sludge to pass into anaerobiosis in the denitrification vessel. These questions are amenable to experimental inquiry and they should be given prompt attemtion in the future.

Anaerobic Sludge Digestion

The digestors were operated for two months, during which time they received about thirty-five 100-ml portions of settled sludge. Volume was maintained constant by dedecanting off liquor after settling the sludge in the digestors. Table XIX gives the time course of build-up of solids in the digestors.

Over the two-month period, the mixed liquor suspended solids built up from 8.2 to 9.3 gm/L in the control digestor. In the digestor fed iron-rich sludge, the solids built up from 14.8 to 20.1 gm/L. Both digestors were originally charged a month previous to the period reported with 400 ml of heavy digestor sludge plus 2500 ml of water, the solids level in both digestors being initially about 7.0 gm/L. During the period reported in Table XIX, the control digestor received about 36 grams dry weight of sludge, and the iron-rich digestor received about 40 grams. Table XX summarized the sludge digestion data.

The specific digestion rate is of special interest; it should be noted that it is independent of volume and sludge concentration. The specific digestion rate designates the fraction of resident sludge that can be digested in a day. In other words, about 2% a day in the control and slightly less than 1% in the iron-rich digestor.

Anaerobic Sludge Digestor Decantate

We have already discussed the COD and BOD quality of the decantates. The phosphate and iron contents of the decantates are given in Table XXI.

The difference in phosphorus content between the control and the iron-rich digestor decantates is quite striking, while the relatively small difference in iron content is surprising. We hasten to point out that even though analyses were run on decantates and filtrates, it would be incorrect to conclude that the contents shown represent iron and phosphate in solution. Decantates (actually coarse-paper filtrates in some cases) are quite turbid and the analytical methods used release iron and phosphate into solution from particles in the sample. The control liquor filters extremely poorly; in fact,

TABLE XIX

Anaerobic Sludge Digestion in Digestors
Fed 100 ml Sludge Approximately Daily

Elapsed Time (days)	Mixed Liquor Suspended Solids (gm/L)	
	Control	Iron-rich
0	7.8	14.8
3	7.6	13.8
7	7.4	14.2
10	10.0	15.0
	8.2	14.5
14	8.4	10.8
16	9.6	15.0
21	8.4	14.0
	9.1	13.3
24	9.0	15.6
27	8.0	15.2
29	8.6	15.8
	8.2	15.5
33	9.0	15.0
36	8.2	17.2
41	9.8	17.8
	9.0	16.7
46	8.0	16.2
49	10.0	18.6
	9.0	17.4
53	--	20.6
56	9.5	----
59	9.0	19.6
	9.3	20.1

The table shows day-by-day values and averages over 10-day periods.

TABLE XX

Summary of Anaerobic Sludge Digestion Data

		Control	Iron-Rich
I	Range of dry suspended solids fed (gm/100 ml)	0.5-2.1	0.4-2.2
II	Average of dry suspended solids fed (gm/100 ml)	1.04	1.15
III	Total for 35 100 ml portions (gm)	36.4	40.2
IV	Average daily feed (III/60) (gm/day)	0.60	0.67
V	Initial total resident dry sludge (gm)	23.8	42.0
VI	Final total resident dry sludge (gm)	27.0	58.3
VII	Sludge increase in 60 days (gm) (VI-V)	3.2	16.3
VIII	Average daily increase in dry sludge (VII/60) (gm/day)	0.05	0.27
IX	Average daily sludge digestion (IV-VIII) (gm/day)	0.55	0.40
X	Specific digestion rate (gm/day. gm (IX/ (VI + V) /2)	0.022	0.008

it doesn't centrifuge very well. The iron-rich liquor both filters and centrifuges remarkably well. The lower phosphorus content of iron-rich decantate can thus be attributed partly to higher iron and partly to improved filterability. Another extremely striking difference between the two digestors is odor. The control digestor odor is about as foul as can be imagined, typical of an anaerobic sludge digestor. The iron-rich digestor has a mild odor reminiscent of crude petroleum.

Digested Sludge Disposal

Time did not permit any experiments on sludge drying or incineration, but samples of both control and iron-rich sludge have been frozen and saved for future work. Certain things can be said,

however, even without experimental evidence. First, the iron-rich digested sludge is no doubt largely a mixture of ferrous oxides and ferrous sulfide probably amorphous in form rather than crystalline.

TABLE XXI

Characteristics of Anaerobic Sludge
Digestor Decantate

		Control	
		Range	Average
Phosphorus	(mg/L)	8-92	57.6
Iron	(mg/L)	22-69	47.8
COD	(mg/L)	-	4150
		Iron-Rich	
		Range	Average
Phosphorus	(mg/L)	2-15	6.0
Iron	(mg/L)	31-222	118.0
COD	(mg/L)	-	181

In the course of anaerobic digestion sulfates become reduced to sulfides and the sulfhydryl compounds of digested microbial tissue also suffer the same fate.

The land disposal of sludges rich in iron sulfide could pose a problem unless full assurance against oxidation could be provided. Oxidation and leaching of such a sludge dump would produce a leach water similar to acid mine drainage. Incineration of the sludge would produce a quantity of sulfur dioxide, and stack scrubbings would also resemble acid mine drainage. The iron-rich sludge is much higher in iron relative to sulfur than are pyrites, the minerals which produce acid mine water in weathering. In the disposal of acid brine in municipal waste treatment plants, the iron will pass very largely into sludge while the sulfate will move through the plant in decant fractions. The ratio of iron to sulfur in digested sludge should be determined in future work. In any case, digested iron-rich sludge probably has about the same composition as limonite iron ores and as such should be of some, albeit limited, value.

Sludge Conditioning

All methods of sludge disposal are benefited by conditioning or dewatering. Chemical conditioning of sludge by sulfuric acid, aluminum sulfate, ferric sulfate, ferric chloride, and lime was reviewed by Balakrishnan et al (32). Relative dewatering rates more than 100 times the untreated rate have been achieved through the use of the chemicals listed above. We have alluded to the improved filterability by primary sludge, activated sludge, and digested mixed sludge from sewage treatment using lime-neutralized acid brine. Masselli et al (33) have reported that 2000-5000 gal. primary sludge is produced per million gallons of raw sewage and 5000-15,000 gal. activated sludge are produced from the same quantity of primary effluent. Chemical conditioning of sludge uses chemicals in the range of a few hundred parts per million, and thus only a small part of the quantity of acid brine available for use at a municipal wastewater treatment plant would be used in sludge conditioning, but there is no doubt about the potential value of acid brine in sludge conditioning. If acid brine were introduced at the primary stage of sewage treatment, there might not be any need for the sludge conditioning step, as we have mentioned.

Oxidation of Ferrous Iron in AAB by Oxygen

In order to determine the additional aeration capacity needed for the oxidation of ferrous iron in acid brines added to sewage and to determine the rate of the reaction under typical conditions two simple experiments were carried out. In the first, samples of AAB neutralized with lime to pH 5.25 were added to tap water samples saturated with dissovled oxygen. Dissolved oxygen was measured with a YSI model 54 oxygen meter at the beginning of the tests, after 10 minutes, and after 15 minutes. The test jars were left open to the air but were not shaken or stirred. The results are given in Table XXII.

TABLE XXII

Reduction of Dissolved Oxygen by Ferrous Iron

Test #	Ratio of Fe++ to O_2 present (equivalents)	% of O_2 used up in 10 Min.	15 Min.
1	0.9	22	22
2	1.9	--	43
3	3.0	53	57
4	4.2	--	73
5	5.6	70	83

The data in Table XXII can be interpolated to conclude that even under quiescent conditions the dissolved oxygen will be 50% reacted in 5-10 minutes at high oxygen demand levels due to ferrous iron. The actual reaction rate depends upon the concentrations of the reactants and the amount of mixing. At a feed rate of 20% AAB (1000 mg Fe++/liter), the zero-time ferrous iron concentration is 200 Fe++ per liter; for oxidation to be complete in a ten-hour period, 20 mg Fe++/L/hr must be oxidized requiring theoretically 20/7 = 3.0 mg O_2/L/hr. For a four-hour detention time, the oxygen rate requirement would be 7.0 mg O_2/L/hr. With typical activated sludge plants the oxygen supply rate from aeration is more than 100 mg O_2/L/hr.

In a second type of experiment, a two-liter sample of AAB-I was neutralized with lime and added to an eight-liter batch of freshly fed activated sludge. The mixture had a pH of 6.8. The mixture was then aerated in our standard AS set-up. Small samples of the culture were taken at intervals, filtered through a membrane, and the filtrate was analyzed for iron. At pH 6.8, it can be assumed that only ferrous iron would remain in solution. The change in soluble iron content with time is shown in Table XXIII and Figure 5.

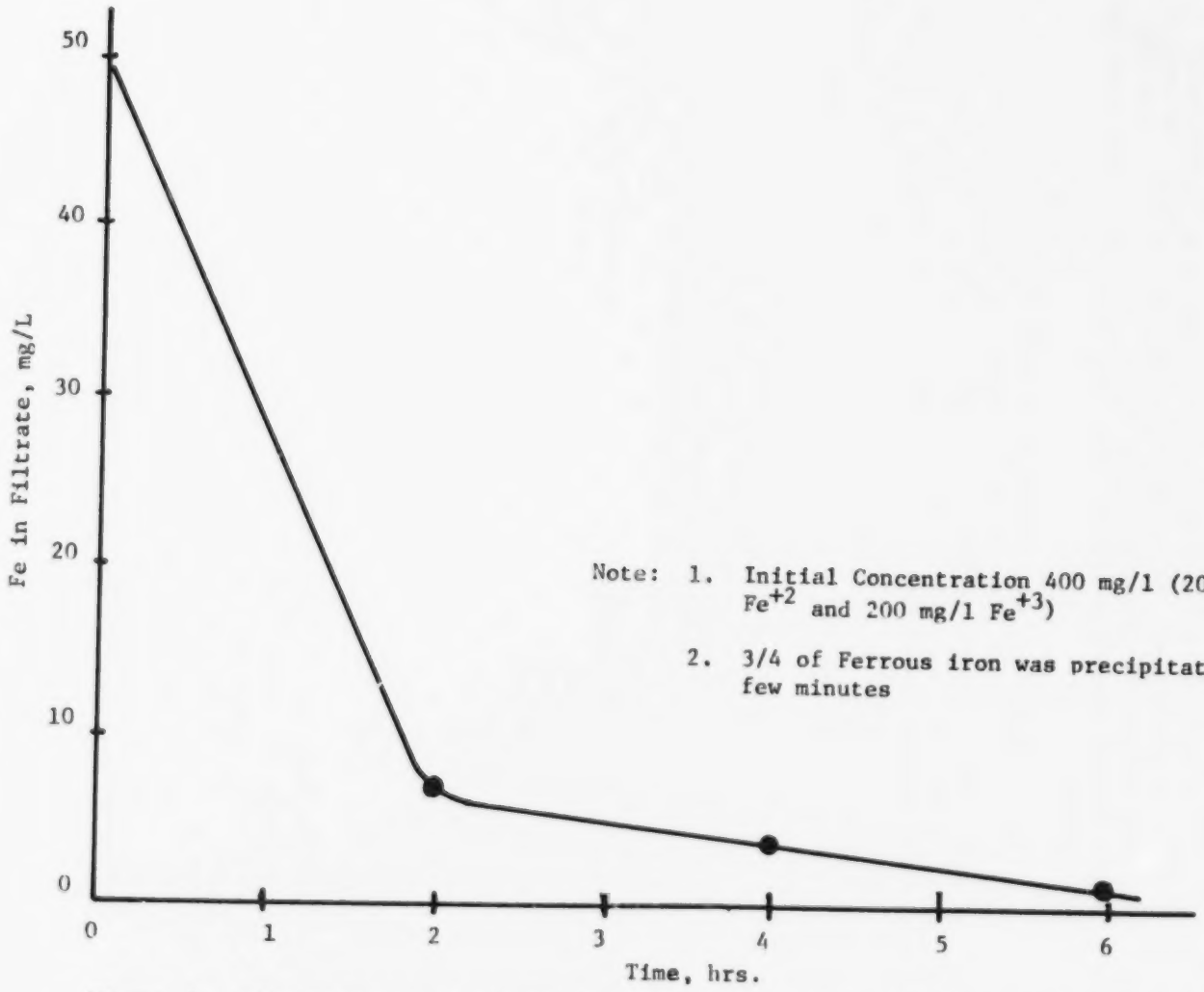
TABLE XXIII

Change in Time of Soluble Iron in AS containing 20% Neutralized AAB

Time (after neutralizing) (hours)	Fe in Filtrate (mg/L)
0	50
2	6.3
4	3.8
6	1.0

It should be noted that the ferrous iron content of the mixture was initially 200 mg/L; thus, three-fourths of the ferrous iron was oxidized and precipitated or was scavenged by the precipitated ferric hydroxide floc in the few minutes required for neutralizing the AAB, sampling the AS mixture, and filtering the sample. From the color change in the AS mixture from greenish brown to orange brown almost all of the ferrous iron added was oxidized (and precipitated) in the first few minutes of aeration.

The aeration requirements in engineering terms are given in Table XXIV and Figure 6.



Note: 1. Initial Concentration 400 mg/l (200 mg/l Fe^{+2} and 200 mg/l Fe^{+3})

2. 3/4 of Ferrous iron was precipitated in a few minutes

Figure 5. Disappearance of Soluble Iron in AS Containing AAB Neutralized with Lime

TABLE XXIV

Oxygen and Work Requirements for Oxidation of Ferrous Iron in Acid Brine

Fe++ (mg/L)	Increased D.O. Requirement (mg/L)	Increased Work Requirement H.P. Hr.
5	0.7	0.125
10	1.4	0.25
25	3.5	0.625
50	7.0	1.25
100	14.0	2.5
200	28.0	5.0
500	70.0	12.5

Assumptions:

1. Stoichiometric relation is one equivalent oxygen per equivalent iron. In English units: one pound of oxygen oxidizes seven pounds of ferrous iron.

2. Aeration efficiency is 2#O_2/H.P.Hr.

3. 1.0 mgd capacity.

Actual aeration requirements would be slightly, but only slightly, higher because of the speed of the oxidation reaction in relation to detention times in actual practice.

Microbiological Status of AAB AS Cultures

The term iron bacteria has been used variously to describe microbes associated with iron oxide crusts or deposits in water, soils, and in man-made systems. In the general sense in which the term, iron bacteria, is used in Standard Methods, both autotrophic and heterotrophic forms are included. In the former instance carbon dioxide is fixed with energy derived from oxidation of ferrous iron, and in the latter instance, some form of organic carbon is assimilated. Heterotrophic bacteria can also bring about the precipitation of hydrous iron oxide by digesting the organic ligand from soluble ferric chelates, or the surfact of bacterial colonies can simply serve as a nucleus for the precipitation of ferric hydroxide

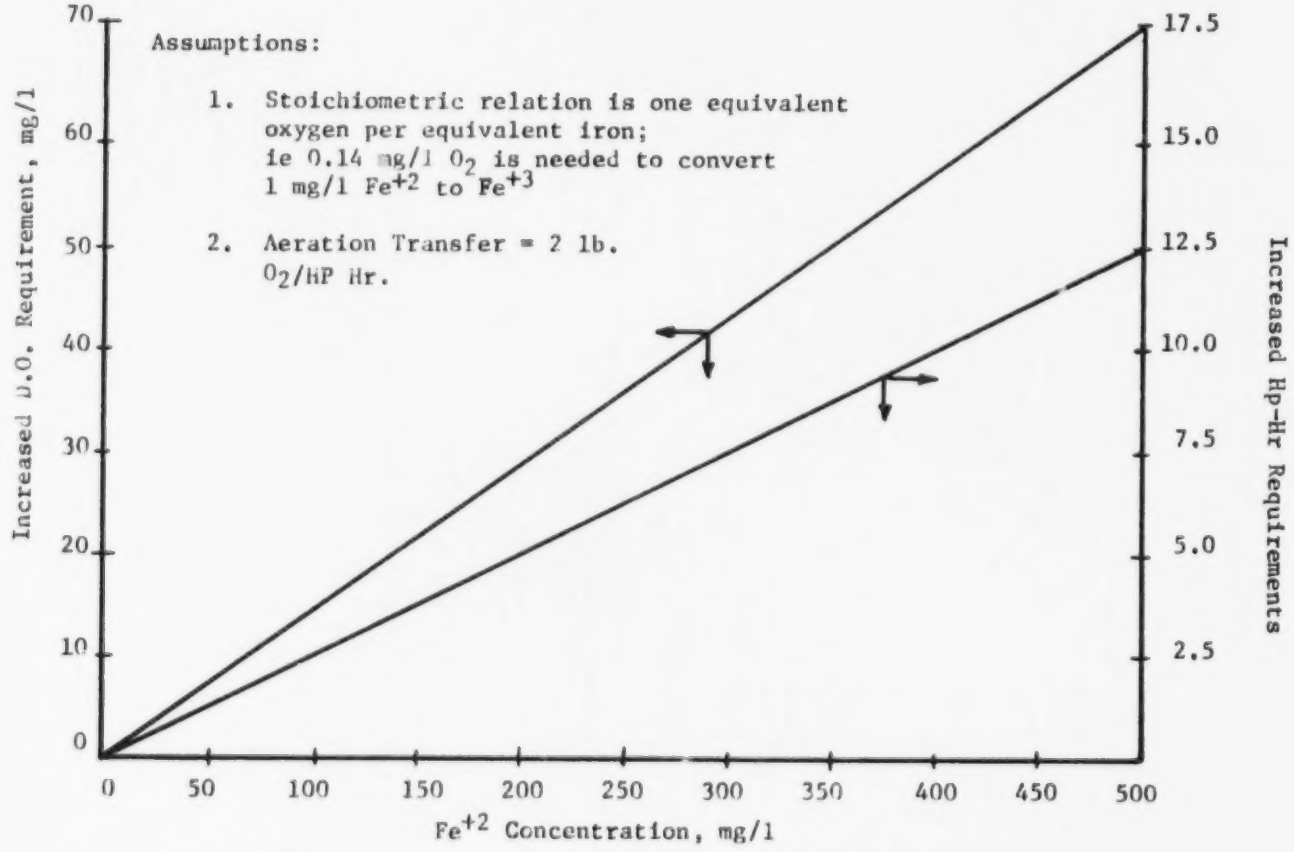


Figure 6. Theoretical Oxygen Requirements For Oxidation of Ferrous Iron

formed by chemical oxidation of ferrous iron in solution. Metallic iron and pyrites (FeS_2) are attacked by natural waters, especially if the water contain dissolved oxygen. Iron bacteria are often if not always associated with the dissolution or corrosion process in nature. The special role of iron (and sulfur) bacteria in the formation of acid mine waters from pyrite was very recently elucidated by Baker and Wilshire (34). Those authors pointed out that Ferrobacillus ferrooxidans oxidizes only ferrous iron, Ferrobacillus sulfooxidans oxidizes $S^=$ and ferrous iron, and Thiobacillus thiooxidans oxidizes only $S^=$ (and thiosulfate). All three of these autotrophic bacteria are capable of growing in media with a pH as low as 2.0, but that capability has not been shown for the some dozen of other species described as "iron bacteria".

Pringsheim (35,36,37) demonstrated that the "sewage fungus" Spaerotilus natans can grow as autotrophically as an iron bacterium, and Skerman et al (38) demonstrated that species' ability to grow as a "sulfur bacterium"; thus it seems to have the same range of chemoautotrophic capability as Ferrobacillus sulfooxidans. The taxonomic status of many microbial entities, described as iron bacteria, is problematical as witnessed by Lundgren's (39,40,41) reference to Thiobacillus ferrooxidans as a participant in acid mine water genesis.

Baker and Wilshire in their studies on pyrite dissolution and oxidation found a variety of ordinary aerobic heterotrophs in their reactors, and they concluded that these microbes, (Penicillium, Pseudomonas, Aerobacter) growing on organic moieties contained in the coal particles associated with the pyrites, play a significant role in the genesis of acid mine water by supplying carbon dioxide to the autotrophic iron bacteria; at low pH carbon dioxide is far less soluble than it is near neutrality.

In summary, chemoautotrophy in iron bacteria, postulated by Winogradsky in 1922, was unproven in 1949; a large number of filamentous iron bacteria are referrable to Sphaerotilus natans, an obligate aerobic variable species which grows perfectly well heterotrophically but does not tolerate low pH. At pH close to neutral, ferrous iron is oxidized so fast chemically by dissolved oxygen that it is doubtful that microbes can avail themselves of the energy. Pringsheim did not rule out the possibility, however, and he pointed out especially that Sphaerotilus in nature grows where ferrous iron, often complexed with humates, is to be found in oxygenated water. At pH 2-3 ferrous iron is oxidized very slowly by dissolved oxygen except in the presence of a bacterial catalyst. Chemoautotrophy in Ferrobacillus sp., which grows at pH 2-3, was convincingly demonstrated by Lundgren and colleagues in the fifties, and the point was further amplified by them in several papers in the sixties (14,15,42,43).

Our own work on the role of iron bacteria in activated sludge fed AAB consisted of attempts to isolate Ferrobacillus from the AS cultures using Silverman & Lundgren's medium (15) and following procedures outlined by them. Both control AS cultures and AAB-AS cultures yielded a mixture of heterotrophs, including pleomorphic molds, and iron bacteria in Silverman & Lundgren's medium. The granular and crusty deposits formed in the iron bacteria cultures was in every way reminiscent of the material called "yellow-boy" in acid mine waters. Our experience with small iron-bacteria cultures using an acid medium containing ferrous iron correspond very well with those of Baker & Wilshire (34), who used a continuously flowing pilot plant with pyrite as the reduced iron source. In their case, the growth of heterotrophic microbes was supported by coal substances and in our case we are forced to conclude that the substrates were substances leached from new polyethlene stock solution bottles--the medium we used contained no organic substrates in its recipe.

As far as the identification or enumeration of Ferrobacillus spp is concerned, we have not succeeded in obtaining growth on the solid medium recommended for that purpose by Lundgren & Schnaitman (42) from AS cultures or from the inorganic liquid enrichment cultures derived from them. It is quite clear, however, that inoculated liquid cultures form yellow-boy in a few days and uninoculated flasks do not. In any case, this discussion of the physiology and ecology of iron bacteria is academic in the present context; activated sludge at neutral pH does not provide the environment for the growth of chemoautotrophic iron bacteria, even though they obviously survive in the environment. Since that group of microorganisms grows autotrophically by the oxidation of ferrous iron, sulfur or sulfide, there is no reason to believe that they should be important in the economy of AS.

Wuhram (20) pointed out another, more important, microbiological consequence of high iron in activated sludge. He observed that iron in excess of 10 mg/L caused the complete disappearance of the protozoan fauna within two days. In his work, technical grade iron salts were used; thus, toxicity from contaminating heavy metals cannot be ruled out as the cause of the disappearance. Our control AS cultures characteristically contained three types of protozoa, small fast-moving flagellates, small and medium-sized motile ciliates, and large flash-shaped stalked ciliates (vorticellids). AAB-fed AS cultures contained no protozoa except for a problematical large subspherical "amoeba" with a very dense granular protoplasm, blunt pseudopodia, and a conspicuous rind or plasmalemma. These "amoeba" change shape very slowly (if at all); these objects may be immature mold sporangia, but no mycelial strands were evident in the culture.

Protozoa in AS play a manifold role. Through predation they remove bacterial strains that might otherwise build up to the detriment of the system. In addition they are responsible for the digestion of a part of the organic load and the assist in flocculation.

The latter function is probably exercised by small, dense excretory particles from the protozoa acting as "cement bridges" between larger, less-dense particles, mostly clumps of bacteria. The loss of protozoa in AAB-fed AS need not be particularly detrimental, however, because of the physico-chemical flocculative action of the iron hydroxide particles, but the absence of protozoa could have a long-term detrimental effect because of the lack of cropping of undesirable bacterial strains.

Concentration of AMD by Reverse Osmosis

Reverse osmosis has been chosen as the process of concentrating acid mine drainage effluent to acid mine drainage effluent to acid brine because of the following reasons:

1. Process is feasible at reasonably economic levels.

2. The potential for considerable reduction in the cost of of concentration is high due to the anticipated improvement in the membrane science and technology.

The flow chart for the concentration process is shown in Figures 7 and 8. The total dissolved solids (TDS) level of the acid mine drainage effluent is assumed at 50 mg/l. The TDS level of concentrated acid brine at the end of two stages is 675 mg/l and concentration factor is about 13. With the addition of third stage reverse osmosis unit, the TDS of concentrated acid mine will be about 2400 mg/l resulting in a concentration factor of close to 50.

The unit cost figures were taken from the information published by Channabasappa and Harris in Industrial Water Engineering (44). These cost figures were adjusted for second and third stage reverse osmosis units to allow for the type of membranes to be used, pH adjustment etc. The costs of concentrating acid mine drainage effluent to 675 mg/l TDS and 2400 mg/l TDS are calculated for plant sizes 1 and 10 MGD as follows:

1 MGL Feed

Cost for the first stage is assumed at 55¢/1000 gallons product water. Allowing 10% and 50% increase for the second and third stage respectively over the first state the unit costs for the second stage is 61¢/1000 gallons product water and 83¢/1000 gallons product water for third stage.

(1) To achieve a concentration of 675 mg/l, two stages of R.O. units have to be employed. The cost for the two stages:

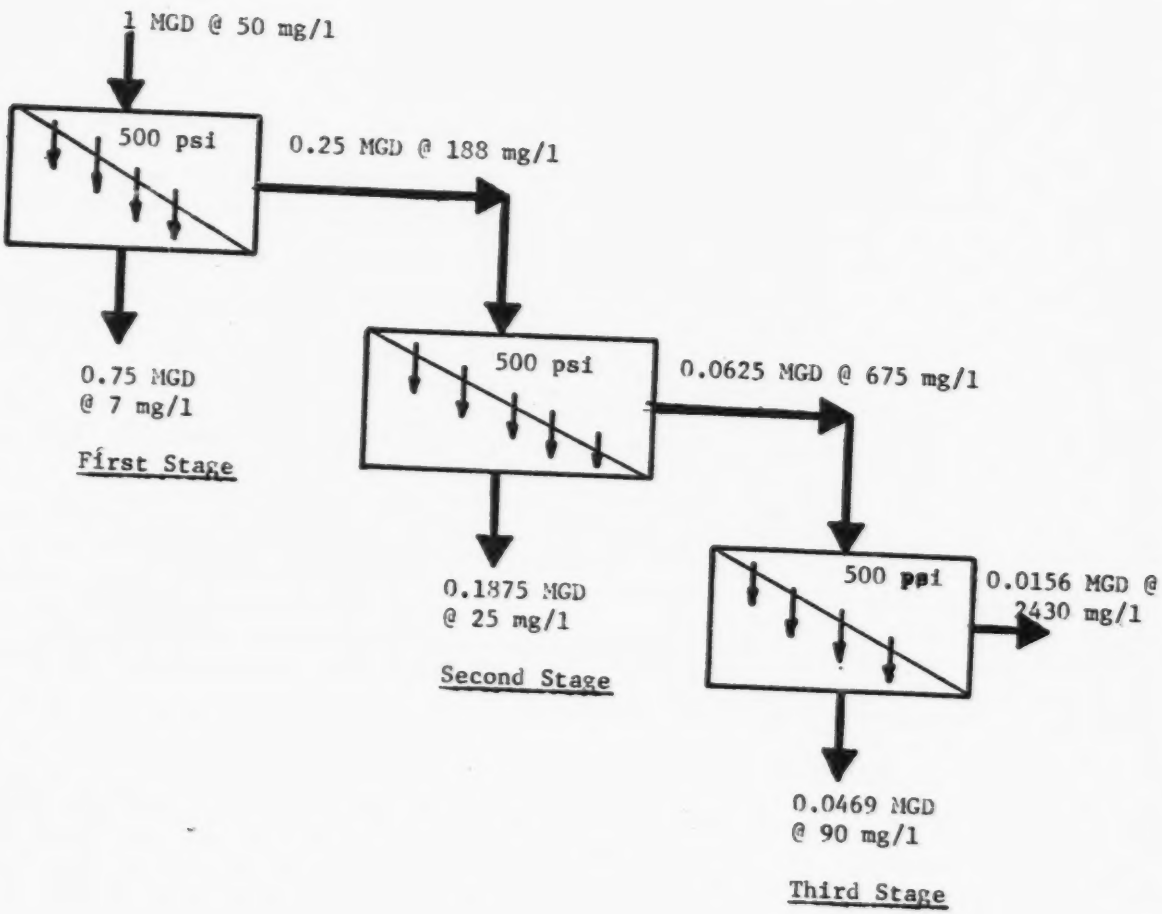


Figure 7. Flow Diagram for Concentrating of AMD - one MGD Plant

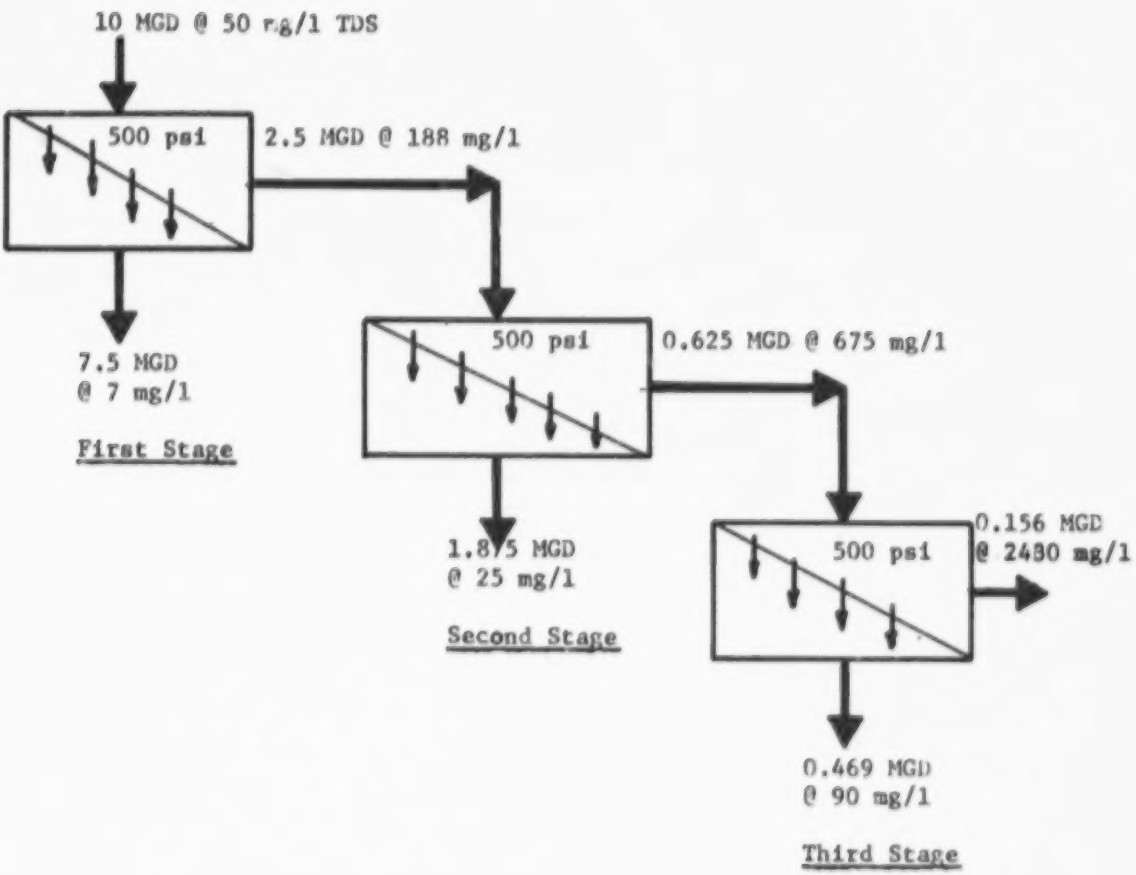


Figure 8. Flow Diagram for Concentrating of AMD - 10 MGD Plant

$= \frac{\$0,55}{1000\ gal}\ (750,000) + \frac{\$0,61}{1000\ gal}\ (187,500)$

$= 413 + 114$

= \$527 / 62,500 gallon of concentrated AMD.
Cost of producing 1000 gallons
of concentrated AMD @ 675 mg/l $= \frac{\$527}{62,500}\ (1000)$

$= \$8.45$

(2) For the concentration of acid brine to 2400 mg/l, three stages have to be employed. The total cost for all the stages:

$= \frac{\$0,55}{1000\ gal}\ (750,000) + \frac{\$0,61}{1000\ gal}\ (187,500) +$

$\frac{\$0.83}{1000\ gal}\ (46,900)$

$= 413 + 114 + 39$

= \$566/15,600 gallon of concentrated AMD
Cost of producing 1000 gallons of
concentrated AMD @ 2400 mg/l $= \frac{\$566}{15,600}\ (1000)$

$= \$36.4$

Cost of Transporting by Tank Truck

Source: 1. McCormack T.I. Trucking Co., Inc.
Bulk Liquid Transporters
U.S. Highway No. 9
Woodbridge, New Jersey
201-382-4800

2. MatLac Pennsylvania - 215-CL9-9800
Trucking Charges up to 100 miles
23.5 cents/100 lb on a minimun of 40,000 lb.
27 cents/100 lb for 40,000 lb.
Cost of transporting by tank trucks
1000 gallons $= \frac{23.5}{100} \cdot \frac{1}{100}\ (8340)$

= \$19.60

Transporting by Rail

Source: Reading Pennsylvania Railways
212-349-2175
For distances less than 10 miles,
$\frac{\$0.58}{100\ lb}$ (8340 lb) = $48.5/1000 gallons
For distances more than 10 miles
$\frac{\$0.49}{100\ lb}$ (8340 lb) = $41.00/100 gallons
For bulk transportation and an extended period, special reduced rates could be obtained by writing to the railways.

Cost of Transporting Brine via Pipeline

The volume of concentrated brine considered for transporting is in the range of 10,000 gpd to 250,000 gpd. The distance to be transported is in the range of 10 to 50 miles. The cost figures for the four cases are determined as below:

Case 1

10,000 gpd - 50 miles
From a preliminary engineering analysis, a 4"ϕ reinforced plastic pipe and 8 hours pumping are selected.

A. 50 miles, 4"ϕ reinforced plastic pipe
@ $1.40/ft. = (5280) (50) (1.40) = $268,000

B. Cost of pumphouse 5,000

C. Cost of pumps and motors 2,000

D. Excavation and filling 3' x 3'
section assumed. Volume =
(5280) (50) (3 x 3) /27 = 88,000 cu. yd.
@ 55 cu. yd/hr., hrs. of backhoe operation
= $\frac{88,000}{55}$ = 1600 hrs. or 200 days

Backhoe and operator @ $320/day 200 x 320 = 64,000
2 laborers @ $50/day x 200 days = 20,000
84,000

84,000

Total Capital Cost 359,000

Contingencies @ 15% 54,000
413,000

Engineering @ 10% 41,300
454,300 or 455,000

Amortizing the capital cost for 20 yr life and 5% interest, annuity cost = $455,000 \times (8.024)\ (10^{-2})$

= 36,500

Daily cost = $\frac{36,500}{365}$ = $100.00

Power: 5HP @ $\frac{1\ ¢}{HP\ hr.}$ 24 hr/day = 0.50

Maintenance @ 2 hrs. operators time/day at $100/day) = 25.00

Total operating Cost 125.50

Cost for pumping 1000 gallons) = $\frac{125.00}{10,000}$ (1000)

50 miles) = $12.55

Case 2

10,000 gpd - 10 miles

A. 10 miles, 4"ϕ reinforced plastic pipe @ $1.40/ft. = 10 x 5280 x $1.40 = 53,600

B. Pumphouse 5,000

C. Pump and motor 2,000

D. Excavation and refilling 1/5 (84,000) 16,800

Subtotal 77,400

Contingencies @ 15% 11,600

89,000

Engineering @ 10% 8,900

Total Capital Cost $97,900

Amortizing capital cost for 20 yr. 5% interest annuity cost = $97,900 \frac{(8.024 \times 10^{-2})}{365}$ = $ 21.60

Power 0.50

Maintenance as in Case 1 25.00

Total operating Cost $47.10

Cost for pumping 1000 gallons) -10 miles) $\frac{47.10}{10,000}$ (1000)

= $4.71

Case 3

250,000 gpd - 50 miles
Pipe size selected = 8"ϕ reinforced plastic pipe

Pumping hours = 24 hrs.

HP = 25

A.	50 miles, 8"ϕ reinforced plastic pipe @ 5.25/ft. = 50 (5280) (5.25) =	$ 1,390,000
B.	Pumphouse	10,000
C.	Pump and motor	5,000
D.	Excavation and filling	84,000
	Subtotal	14,789,000
	Contingencies @ 15%	223,000
		1,712,000
	Engineering @ 10%	171,000
	Total Capital Cost	$ 1,883,200

Amortizing @ 5% interest, 20 yr. life
annuity cost = $\frac{1,883,200\ (8.024 \times 10^{-2})}{365}$ = $ 415.00

Power, 25HP 6.00

Maintenance
4 times @ 2 hr/each time) $ 100.00
operator @ $100/day

Total operating Cost $ 521.00

Cost of pumping 1000 gallons) of acid brine - 50 miles) = $\frac{521}{250,000}$ (1000)
= $ 2.10

Case 4

250,000 gpd - 10 miles
assumptions same as in 3

A.	50 miles, 8"ϕ , @ $525/ft	$ 278,000
B.	Pump and motor	5,000
C.	Pumphouse	10,000
D.	Excavation	16,800

Subtotal	309,800
Contingencies @15%	46,200
	356,000
Engineering @ 10%	35,600
Total Capital Cost	$ 391,600

Amortizing for 20 yrs 5% interest

$$\text{annuity cost} = \frac{391\,600\ (8.024 \times 10^{-2})}{365} = 86.00$$

Power	2.00
Maintenance as is Case 3	100.00
Total operating Cost	$188.00

Cost of pumping 1000 gallons of acid brine - 10 miles $= \frac{188}{250,000}\ (1000)$

$= \$0.75$

The costs of pipelining are shown in Table XXV. In that table the numerator figures are the costs per thousand gallons for the distances shown, and the denominator figures are the cost per thousand gallons per mile for the plant sizes shown.

TABLE XXV

Pipeline Transport Cost Estimates

Plant Size	Distance	
	10 miles	50 miles
10,000 gpd	$\frac{\$4.71}{0.47}$	$\frac{12.55}{0.25}$
250,000 gpd	$\frac{0.75}{0.075}$	$\frac{2.15}{0.043}$

SECTION VIII

SUMMARY

This report examines the feasibility of concentrating acid mine waters by certain processes and transporting the concentrated brine to municipal wastewater treatment plants for disposal. Relatively pure water is a by-product of the acid mine water treatment, and the iron-rich acid brine is of some value in sewage treatment. The artificial brine used in the laboratory research was devised to simulate a fifty-fold concentration of acid mine water with respect to iron and acidity, (2000-10,000 mg Fe/L and acidity 7,800-23,000 mg/L as $CaCO_3$).

In experiments on primary settling acid brine was added at levels up to 50% vol/vol with no significant effect on the process. With acid brine neutralized with lime, a marked improvement in primary settling was found. In addition, virtually 100% removal of phosphate is achieved.

Activated sludge digestion was found to be completely inhibited by acid brine at the levels included in this study, but lime-neutralized brine was not particularly inhibitory. Over a two-month period the control activated sludge culture achieved as high as 89% removal of COD and averaged 71% removal. The activated sludge culture fed 20% vol/vol lime-neutralized acid brine achieved as high as 90% COD removal and average 64%. The corresponding averages for BOD removal were 90% in both the control and the acid brine activated sludge units.

Anaerobic sludge digestion was studied using the daily harvests from control and acid brine-fed activated sludge units over a two-month period. The specific digestion rate in the control digestor was 2% per day and 1% per day in the digestor fed iron-rich sludge. Both digestors produced a decantate that was readily digested by activated sludge. In contrast to the control anaerobic digestor, the iron-rich digestor produced a decantate that was low in phosphate, low in COD, and virtually odor-free.

Oxygen and work requirements for oxidation of ferrous iron in acid brine were determined to be 0.14 mg oxygen per milligram ferrous iron and 0.025 horse power hour per milligram ferrous iron in a one-mgd plant. Thus in a one-mgd plant handling acid brine and having 500 mg/L ferrous iron in the plant flow, the work requirement for pumping air to oxidize the ferrous iron is 12.5 horse power hour.

The microbiological status of the acid brine activated sludge unit was monitored along with the control. Activated sludge at neutral pH does not provide a suitable environment for the growth of chemoautotrophic iron bacteria, but they can be isolated from such

cultures. As had been previously observed in Switzerland where iron salts are used for nutrient removal in sewage treatment, protozoa were absent from our acid brine-fed activated sludge unit. Their absence, however, did not cause any impairment of flocculation in the sludge.

Reverse osmosis offers an attractive method for concentrating acid mine water. The process produces a concentrated brine and a relatively pure water as a by-product. A three-stage system could produce a brine of 24000 mg TDS/L from acid mine water containing 50 mg TDS/L - a concentration of about fifty-fold. The cost of brine production in a 1-mgd plant is estimated to be $36.40/1000 gal. brine or 76¢/1000 gal. acid mine water treated. The process will produce 47,000 gal. pure water for every 1000 gal. of brine produced.

Pipeline transport of the brine from the mine site to municipal sewage treatment plants is estimated to be cheaper than truck or rail, but the pipeline method requires a capital outlay, right-of-way purchase, and construction. Tanktruck transportation costs would be on the order of $20.00 per 1000 gal. for up to 100 miles. Standard rail rates would be roughly twice that amount, but bulk rates and an extended contract would permit a reduction of the rate. The pipeline transport costs, not including costs for right-of-way but including amortization of other capital outlay, are estimated to be in the range of $4.30 per thousand gallons for a one-hundred mile pipeline of 250,000 gpd capacity.

SECTION IX

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SECTION X

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27 Abstract

Laboratory scale studies were carried out to evaluate the disposal methods for concentrated acid mine drainage in the municipal waste treatment. The studies indicate that the concentrated acid mine drainage produced, are not of sufficient value to pay for treatment by any known method, but they can be disposed of through municipal wastewater treatment plants, where they will be of some value especially in sludge conditioning and nutrient removal.

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